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# **Research Article**

# DEVELOPMENT OF A COMBINED TECHNOLOGY (SORTING/COMPOSTING/SOFT PYROLYSIS - SCP) FOR THE RECOVERY OF MUNICIPAL SOLID WASTE WITH ZERO WASTE DISPOSAL IN LEBANON AND DEVELOPING COUNTRIES

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### ABSTRACT

This paper aims to develop an alternative complete technology and to assess its potential to manage municipal solid waste (MSW) properly to reach the state of zero waste disposals in Lebanon and developing countries. Meanwhile, Lebanon continues to face serious MSW management challenges associated with urbanization and the absence of a reliable policy plan. Thus, two different sorting modes were followed to prepare two categories of MSW samples: (i) samples A correspond to MSW from which only recyclable materials are removed and (ii) samples B correspond to MSW from which recyclable materials and food waste are removed, whereas samples A and B were thermally treated at low temperature. The conditions of catalytic thermal treatment were studied, and the effects of many parameters such as nature and rate of catalysts and additives, heating rate and maximum heating temperature on the yield of different pyro-products were examined.

Interesting pyrolytic conditions were optimized. They are an oxygen free environment, a heating rate of 2.5 °C min<sup>-1</sup> during six hours and low temperature of 300-350°C at which the disintegration of carbon chain start, sodium hydroxide (1%) as catalyst and Calcium carbonate (2%). Obviously, under these operating parameters, the volume of gas flux was reduced, volatilization of heavy metals trapped in solid phase and formation of dangerous substances were avoided and poisonous gases were neutralized by additives. Thus, emission control is easier; operating and maintenance costs are greatly reduced. This process is called soft pyrolysis.

Under soft pyrolysis conditions, high yield of pyro-water (55 %) and low yields of energy carrier pyro-products (oil 4.5 % / char 21 %) were obtained after the pyrolysis of samples A, inversely to the yields obtained using samples B (water 14 % / oil 33.6 % / char 26 %). These results proved the necessity to remove organic materials (food waste, vegetables and plant debris) from MSW before been thermally treated.

Furthermore, pyro-products were physicochemically characterized, and their modes of treatment, recovery and recycling were defined. Before treatment, the analysis of pyro-char showed a carbon rich mixture (55%) and a high content of ash (45%) including eventual pollutants (salts, heavy metals,...). Several interesting uses of pyro-char have been tested successfully such as its incorporation in asphalt roadway paving operation in a fractional ratio 1/10, or after treatment as energy carrier (calorific value = 20071 KJ/Kg) and feedstock in chemical industry. The analysis of the derived pyro-oil indicated that it is chemically complex, composed of a mixture of different hydrocarbons, with an increasing viscosity along the pyrolysis process. The pyro-oil is water free and characterized by a high calorific value (39 000 kJ/Kg), presenting a good fuel for internal use as well as for external. Moreover, the generated wastewater (pyro-water) was analyzed and treated properly. Non-condensable fraction (syngas), volatile hydrocarbons can be used as an inner fuel in the reactor.

Therefore, combined technology based on three complementary processes in triangular shape (Sorting of recyclable materials and food waste as per sample B - Composting of food waste and vegetables - Soft pyrolysis of the remaining rejects) was defined, satisfying the specificity of developing countries such as limited resources, high content of vegetables (60-70%) in accordance with the environmental restrictions. MSW are converted into giving valuable (recyclable materials, compost, char, oil, ...) and solid residue with many uses leading to zero waste disposal, or simply disposed in safe conditions. These technologies (SCP) could be the convenient treatment methods to solve the acute Lebanese problem of MSW management and may constitute a model of management for developing countries.

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# **INTRODUCTION**

Municipal Solid Wastes (MSW) is a continually growing problem at global and regional as well as at local levels. MSW may be defined as the organic and inorganic waste materials produced by various activities of the society and generated from several sources and which have lost their value to the first user <sup>[1]</sup>.

According to the classification made by the Centre for Environment and development (in EU), MSW is composed of solid waste based on origin (e.g. food, demolition and construction, and agricultural waste), characteristics (i.e. biodegradable and non-biodegradable) and risk potential (i.e. hazardous waste and non-hazardous wastes) <sup>[2]</sup>. The Management of solid waste may be defined as that discipline associated with many coordinated activities such as the control of generation, reduction, collection, transfer, processing, and disposal of MSW<sup>[3]</sup>. The management of MSW has become an acute problem due to enhanced economic activities and rapid urbanization. The treatment of MSW adopted by a proper and sustainable way can lead to many benefits such as recovery and valorization of waste and support of economic development with respect of the best principles of public health, and other environmental considerations. The main objective of Sustainable waste Management (SWM) is the treatment that involves different techniques mainly biological (as anaerobic digestion and aerobic composting) and thermal treatment (incineration, gasification and pyrolysis) that are called conversion technologies (CT)<sup>[4]</sup> (Figure 1).

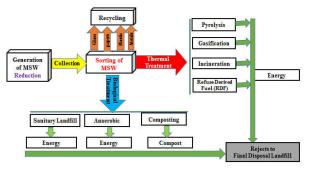


Figure 1 Overview about General management of MSW.

Currently in Lebanon, the government and population are facing a growing problem with the generation of approximately 6000 tons of MSW per day which make up more than 80 % of the total solid waste stream generated in Lebanon<sup>[5]</sup>. At present, approximately 58 % of all MSW is generated in Beirut and Mount Lebanon, followed by 16 % in North Lebanon, 15 % in South Lebanon and Nabatieh and 11 % in the Bekaa<sup>[6]</sup>. Despite the growing interest of the government in recent years to handle this problem in a safe and hygienic manner, landfilling in no sanitary conditions and opened dumps with more than 600 dumping sites are scattered in various areas of Lebanon, are the main disposal method covering an estimated 83 % of generated MSW, and till now no final plan is established to counter this scourge, with all consequences on the environment and human health <sup>[7,8]</sup>. Approximately 8 % only of MSW in Lebanon are recycled and 9 % are composted in many plants (Beirut, Tyr, Baalbek,...), in which organic waste is converted into manure and fertilizer to be sold to agricultural activities <sup>[6]</sup> (Figure 2,b). But unfortunately the quality of products containing rejects and undesirable materials is very bad limiting their use by agriculture sector.

As in all developing countries, MSW in Lebanon is characterized by a high content of organic matter (60-75 %) (Figure 2, a). Modern technologies of MSW treatment were studied taking in considerations the composition of MSW, the limitation of opened surface and financial resources. Effectively, when MSW are collected and delivered then different types of materials must be sorted into different fractions. Sorting is a process in which the wastes are separated into three categories suitable for different end uses <sup>[9]</sup>. First category is composed of recyclable materials such as paper and cardboards, metals, plastic/rubbers <sup>[10]</sup>. Second category is vegetable matter which can be further processed by anaerobic or aerobic ways to produce methane or fertilizer, respectively. Third category is composed of all rejects or exhausted materials collected and sent to sanitary landfill <sup>[11]</sup>.

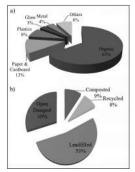


Figure 2 a) The composition of solid waste (%) generated in Lebanon <sup>[6]</sup>, b) The percentage of different methods for MSW management applied in Lebanon <sup>[6]</sup>.

Organic waste sent to composting facilities undergoes several pre-treatment steps before composting. Materials are screened from impurities, often shredded to smaller particle sizes for faster decomposition. Composting is an essential and continuous process where organic, or carbon-based, materials exposed to the elements of nature, particularly air and water, are broken down into smaller compounds by microorganisms. The end product, compost, is an organic material that can be used as a soil amendment or as a medium to grow plants. Mature compost contains a stable, carbon-rich material that may be blended with other organic streams or bulking agents for optimal density, carbon to nitrogen ratio, and moisture levels<sup>[9]</sup>.

Moreover, thermal treatment methods including incineration, gasification and pyrolysis which offer some benefits over landfills means: recovery of energy and reduction of the volume and quantity of waste. However, the remediation costs for air pollution control are usually very high due to the treatment of larger gas volume. With its characteristic to break down the large molecules into smaller ones, pyrolysis has been proven to be a good alternative to the disposal of MSW<sup>[12, 13]</sup>. Pyrolysis process is the thermochemical decomposition of carbonaceous organic matter, in the absence (or very limited supply) of oxygen at relatively low temperatures between 400 °C and 750 °C. During pyrolysis, the organic substances undergo simultaneous changes in their physical state and chemical composition resulting in the formation of a synthetic gas (CO<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>), pyrolysis oil (a bio-fuel) and carbon-rich residue (char)  $^{[14, 15]}$ . The products of pyrolysis can all be used as fuels or indirectly as raw materials for other chemical/material industrial processes. Primarily, three types of pyrolysis reactions have been isolated on the basis of temperature and processing time of the feedstock named slow, flash and fast pyrolysis [16, 17].

Soft pyrolysis is a thermal catalytic treatment distinguished from conventional pyrolysis <sup>[18]</sup> by a lower temperature around 300 °C and nature of chemical additives <sup>[19]</sup>. Soft pyrolysis

process is characterized by several advantages, mainly better control of gas flux. Also, contrary to direct incineration, gasification and conventional pyrolysis<sup>[20]</sup>, soft pyrolysis have demonstrated no possibility of poisonous emissions of matters or chlorinated compounds which are neutralized or trapped in solid phase. Emission controls are easier for soft pyrolysis due to the lower temperature, nature and volume of gaseous emissions which lead to reduce the investment and operating costs. As for conventional pyrolysis<sup>[21]</sup>, soft pyrolysis leads to an important reduction of volume of MSW and formation of valuable products.

This work aimed to select the most convenient pre-treatment process (sorting) and the conditions of thermal conversion (pyrolysis) of MSW, in order to draw an efficient flow for sustainable management of the acute problem of MSW in Lebanon and developing countries. Thus, the conversion technologies for MSW by soft pyrolysis at low temperature (250, 300 and 350 °C) was studied using two types of MSW samples (A & B) prepared by two sorting modes. The yields and the physicochemical properties of pyrolysis products (pyro-water, pyro-oil, pyro-char and pyro-gas) were determined. The effects of different types of catalysts and additives were examined.

# METHODOLOGY

# Samples preparation for pyrolysis

Two categories of samples were prepared from a given quantity of municipal garbage, following two sorting modes:

The first sorting mode corresponds to the remove of all recyclable materials such as glasses, papers, metals, clean plastics, hazardous electronic wastes and batteries. These materials form  $20\pm5$  % of the initial municipal garbage. Whereas, the remaining  $80\pm5$  % are waste and rejects (food waste, vegetables, plant debris, dirty and mixed plastics, and rubber), they are collected together to give the sample A.

However, the second sorting mode starts by the removing of recyclable materials (hazardous electronic wastes, and batteries) forming  $20\pm5$  % of the initial municipal garbage and the food waste, vegetables, and plant debris (60-65±5 %) are conducted to the composting process. At the end of the sorting mode, the  $20\pm5$  % residual materials are collected together to give the sample B.

Samples A and B were separately shredded and homogenized to be ready for thermal treatment. The variation of  $(\pm 5 \%)$  was related to the source and to the composition of the municipal garbage. Garbage contents are different between cities and rural areas.

## Thermal treatment procedure

The thermal treatment of MSW sample was carried out at laboratory scale using a pyrolysis system. This system was built up using a metallic cylindrical reactor (capacity 500 g), a fractional distillation apparatus (condenser tube and a round flask for liquid collection) and a gas scrubber bottle. The reactor was heated by controlled heater equipped with thermocouple (Mantle Heater), and the thermal conversion was performed at relatively low temperature, normal pressure and oxygen free environment. Five hundred grams of MSW sample were introduced into the reactor. The heating was then initiated at a rate of 2.5 °C min<sup>-1</sup> to reach the preset temperature and kept at this temperature until complete thermal conversion (approximately 6 hours). Furthermore, to obtain an inert atmosphere, nitrogen gas was injected across the system for at least 20 min while the temperature is rising till 100 °C.

During the thermal conversion, the condensable phase was collected in a round flask, while the non-condensable phase was drained in the gas cleaning system which is composed of a distilled water bottle. The effects of temperature, catalysts, and additives on the efficiency of the thermal conversion were studied and the characteristics of the by-products were examined. Thus several experiments were carried out at three different preset temperatures (250, 300 and 350 °C), with the addition of 5 g from different catalysts (calcium hydroxide, sodium hydroxide or zeolite) and 10 g from different additives (calcium carbonate or calcium hydroxide).

## Procedure for condensable phase separation

At the end of the experiment, the separation of the condensable fractions was carried out using a separatory funnel. Two fractions were then obtained: (i) an oily fraction called pyro-oil and (ii) an aqueous fraction called pyro-water. These fractions were stored in glass bottles in order to undergo later an appropriate treatment and to be characterized (Figure 3). Moreover, the metallic reactor was allowed to cool down, a solid residue (pyro-char) was then removed and stored for analysis (Figure 3).

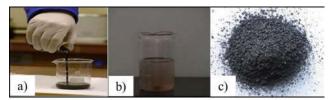


Figure 3 Different fractions of pyro-products: a) oil fraction, b) aqueous fraction and c) solid fraction.

## Treatment of the pyro-water

In order to remove organic carbon from the aqueous phase (wastewater), 50 mL of the pyro-water were treated with ferric chloride (FeCl<sub>3</sub>) as flocculent. Since ferric chloride is much more efficient at basic pH, the pH was adjusted to obtain a basic medium (pH 8-9) using sodium hydroxide. Samples were stirred and allowed to settle for few hours. The obtained precipitate was then removed by filtration using filter paper (0.45  $\mu$ m as porosity) and water became transparent.

# Physicochemical analysis of pyro-water and pyro-oil

The physicochemical properties of pyro-products generated from the thermal treatment of MSW were examined before and after treatment. The pH and electrical conductivity were measured using Orion 4 star/Thermo scientific<sup>™</sup> instrument. The concentrations of dissolved elements were determined by an Atomic absorption spectrophotometer (Perkin-Elmer AAS) and PinAAcle 900T ionic chromatography (Thermofisher Scientific). Dissolved anions (sulfate, nitrite, nitrate, phosphate, and chloride,...) were evaluated by spectrophotometry (Hach Spectrophotometer DR3900). The quantity of total organic carbon was measured by SHIMADZU TOC-VWS. The calorific value of oily phase was identified by calorimeter. Moreover, the chemical composition of the pyrooil was analyzed by gas chromatograph coupled with mass spectrometry (Shimadzu, GCMS-TQ8050).

## Chemical analysis of the pyro-char

The composition, the global calorific value, the humidity and the sulfur content of the pyro-char were measured in the specialized laboratory of Sibline cement factory. Granulometry of pyro-char samples and characteristics of asphalt for roadway prepared by incorporation in a standard formulation were studied in a French specialized laboratory. Measurements and tests were done according to the international standards.

# **RESULTS AND DISCUSSIONS**

## **Optimization of experimental conditions**

The catalytic thermal treatment of MSW samples (A & B) was studied in pyrolytic conditions giving pyro-products (pyro-oil, pyro-water, pyro-char and pyro-gas). Conversion conditions were preset at heating rate of 2.5 °C min<sup>-1</sup>, during six hours, under normal pressure and free oxygen environment. The effects of temperature, catalysts and additives on the decomposition of MSW samples were studied.

## Effects of temperature

Temperature is the key factor in pyrolysis which is one of the alternative technologies for MSW treatment. The effects of the final operating temperature (250 °C, 300 °C and 350 °C) on the pyrolysis and on pyro-products production were studied in the presence of sodium hydroxide as catalyst. The study was limited at 350 °C as maximum temperature, above which higher amount of toxic volatile products may be released. The thermal treatment of samples A and B were carried out under the same conditions; the yields of pyro-products are represented in the figure 4.

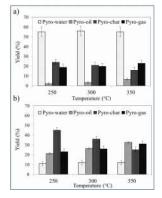


Figure 4 Evolution of the pyro-products yields (%) versus temperature after the pyrolysis of MSW samples A (a) and samples B (b).

The examination of the yields of pyro-products showed the conversion of MSW samples from solid state to liquid and gas one. Moreover, the rate of thermal conversion rises with increasing temperature. The yields of pyro-oil increase by 1.5-2 folds and 1.2 folds for samples A and B, respectively (Figure 4). Whereas, the yields of pyro-char decrease by 1.2-1.4 folds. Furthermore, whatever the preset temperature for the thermal conversion of samples A, 55 % of the pyro-products are pyrowater (Figure 4a). These yields are 5 folds greater than those obtained with samples B (Figure 4b). However, the yields of

pyro-oil are lower by 8 to 10 folds than those obtained with samples B.

These results indicate that the removal of organic materials (food waste, vegetables, and plant debris) from MSW samples (B) before undergoing pyrolysis is crucial, leading to the formation of a higher yield of pyro-oil (21-33 %) and to the release of a much lower quantity of polluted water (12 %).

## Effects of catalysts and additives

The performance of catalysts such as sodium hydroxide and zeolite at 300 °C were studied and results are represented in figure 5. The comparison of their effects on the conversion rate of MSW samples (A & B) is represented Figure 5.

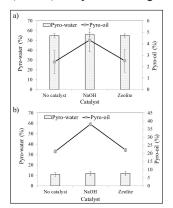


Figure 5 a) Evolution of the pyro-products yields (%) versus catalyst after the pyrolysis of MSW samples A (a) and samples B (b).

It appears obviously that the addition of zeolite as catalyst during the pyrolysis of the samples A and B doesn't have any effect on the conversion rate of MSW samples, whereas, the use of sodium hydroxide increase the rate of pyro-oil formation by 1.8 folds. Moreover, the use of catalysts doesn't influence the rate of pyro-water formation.

The pH of pyro-water was 3.4 due to the formation of acids during pyrolysis. Thus, two percent of bases such as calcium hydroxide and calcium carbonate were incorporated into the reactor in order to inhibit the formation of acids and therefore to protect the facilities from corrosion. The incorporation rate of basic additives was controlled to obtain a pH near the neutrality (pH = 6.7).

## Characterization and treatment of pyro-products

Pyro-water, pyro-oil, pyro-char and pyro-gas are the products of the catalytic thermal treatment of MSW samples at relatively low temperature (300-350 °C). The physicochemical characterization of these products was done to evaluate their properties and to assess the recovery methods with respect to the environmental regulations and economic requirements.

# Pyro-oil

The main parameters of the pyro-oil fraction obtained from the condensable gaseous fraction were analyzed and reported in table 1.

Parameters		Pyro-oil	Light diesel oil <sup>[2</sup>	<sup>2]</sup> Biodiesel <sup>[23]</sup>	
Density (g/cm <sup>3</sup> ) at 15°C		0.89	0.82-0.88	0.86	
pł	pH				
Flash po	Flash point (°C)		> 55	173	
Cloud po		-18	< 2	-1	
Calorific con	Calorific content (KJ/Kg)		> 41500	37270	
Sulfu	r (%)	0.28	< 0.3%	0	
Asp	ect	Dark Brown			
Water and Se	ediment (%)	0.6	< 0.1		
	Fraction at T< 100 °C	12.4			
Fractional distillation (%)	Fraction at T<140 °C	29.5			
	Remaining fraction	57.1			
Miscibility	with water	No	No		
Miscibility w	Miscibility with diesel oil		yes		
Sodium	(ppm)	0.41	< 1		
Potassiur	Potassium (ppm)		< 1		
Cadmium (ppm)		0	< 1		
Iron (J	Iron (ppm)		< 1		
Lead (	ppm)	0			
Calcium (ppm)		0.26	< 1		
Copper (ppm)		0	< 1		
Zinc (ppm)		0.11	< 1		
Nitrates (ppm)		0			
Nitrites (ppm)		0			
Chlorides (ppm)		0			
Sulfates (ppm)		0			
Phosphate (ppm)		0			

**Table 1** Physicochemical characteristics of the pyro-oil obtained after catalytic thermal conversion.

The pyro-oil obtained after thermal treatment is composed of a mixture of various hydrocarbons. The examination of its characteristics indicate that the pyrolytic oil has a flash point (31 °C) much lower than petroleum fuels (60 °C) and biodiesel (173 °C). Furthermore, the pyro-oil has a closer density to the heavy diesel (approximately 0.9), a closer calorific value (39 000 kJ/kg) to petroleum diesel (42 000 kJ/kg) and very low sulfur content (0.28 %).

It can be concluded that the obtained pyro-oil can be composed of a mixture of hydrocarbons with different physicochemical properties, giving a pyro-oil with low flash point. Thus, the physicochemical properties must be improved by distillation to obtain a better homogenous product and a higher flash point. Globally, with a high energetic value closer to light diesel, closer density to heavy diesel, very low sulfur content (0.28 %), low water and sediments percent and heavy metals almost free, this product could be a good fuel for industrial use.

### Pyro-water

Pyro-water is the fraction separated from the condensation of the gas flux formed during the thermal treatment process. A high yield of pyro-water was obtained (> 50 % of the mass of raw material) from the pyrolysis of samples A, explained by the high content of vegetables in the MSW collected from rural areas while it is less than 13% from samples B. The characterization of pyro-water is crucial in order to control the conversion process. Table 2 illustrates the main physicochemical parameters of the pyro-water fraction before and after its treatment by FeCl<sub>3</sub>. In fact, many acids are formed during the pyrolysis of MSW, leading to the generation of an acidic pyro-water (pH = 3-4). The acidity might lead to the corrosion of facilities and affect the preservation and the safety in the plant. The remedial was done by addition of sodium hydroxide or calcium carbonate with a rate 1 % and 2 %, respectively, increasing pH to 6-7.

<b>Table 2</b> Characteristics of the pyro-water before and after
treatment. $NA = not available$

Parameters	Before treatment	After treatment	Limits [24]
Density (g/cm <sup>3</sup> ) at °c	1.04	1	1
pH at 23.8 °C	6.77	5.3	6-9
Conductivity(mcs/cm)at 26°c	938	728	1000
Aspect	Light brown	Colorless	Colorless
Sodium (ppm)	0.6	0.3	NA
Potassium (ppm)	0.6	0.4	NA
Cadmium (ppm)	0	0	0.2
Iron (ppm)	14.14	14.9	5
Lead (ppm)	0	0	0.5
Calcium (ppm)	0.42	0.36	100
Zinc (ppm)	0.34	0.31	5
Total organic carbon (ppm)	487.5	15.6	NA
Copper (ppm)	0.019	0.02	1.5
Nitrate (ppm)	0	0	90
Nitrite (ppm)	0	0	NA
Sulfates (ppm)	4.36	4.54	1000
Chloride (ppm)	328	336	NA

Before treatment, the color of the pyro-water was yellow brown, indicating the presence of pollutants. The values of physicochemical parameters reported in table 2 revealed the presence of an excessive amount of impurities, expressed mainly by the high content of total organic carbon (487 ppm). The treatment of aqueous fraction was carried out by the addition of a ferric chloride solution at pH = 8-9. The drop of pH to reach 4.6 after treatment is due to Lewis acidity of ferric chloride. After treatment, the concentration of total organic carbon decreased by 31 folds to reach 15.6 ppm (table 2). The aspect of the water becomes transparent after been yellow (Figure 6). These results indicate clearly the efficiency of the applied treatment method, and the ability to reuse or discharge the treated water into surface water without been toxic to aquatic life.

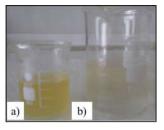


Figure 6 Pyro-water treated by FeCl<sub>3</sub>: a) Before treatment and b) After treatment

### Pyro-char

Pyro-char is a black solid residue, a carbonaceous product obtained by the pyrolysis of organic materials. At low temperature (250-350 °C) and low heating rate process (2.5 °C min<sup>-1</sup>), high pyro-char production can be obtained from the process. At 300 °C, the pyrolysis of samples B give 36 % of pyro-char, while when temperature rise to 350 °C the yield of pyro-char deceases (25 %). Moreover, when samples A are used the yield of pyro-char drops significantly. Thus, the properties and the yield of pyro-char are affected by the properties of parent feedstock and by the applied operating conditions, mainly the heating rate, the maximum preset pyrolytic temperature and the residence time.

In fact, the disposal of the pyro-char represents an easy option, but since the recent environmental restrictions, its characterization and recovery represent a great deal to develop environmental friendly technologies, achieving a maximum recovery rate. The analysis of pyro-char obtained after the thermal treatment of solid fraction was done in specialized laboratory; results are listed in table 3.

<b>Table 3</b> Physicochemical properties of the pyro-char
before treatment.

Parameters		Results
Sulfur (%)		0.4
Gross Calorific va	lue (KJ/Kg)	12095
Net Calorific valu	ue (KJ/Kg)	10670
Moisture (	(%)	0.68
Total ash	(%)	44.86
	SiO <sub>2</sub>	22.60
	$Al_2O_3$	4.70
	Fe <sub>2</sub> O <sub>3</sub>	3.77
	CaO	52.98
	MgO	2.18
Composition of	$SO_3$	2.07
ash (%)	K <sub>2</sub> O	1.53
	Na <sub>2</sub> O	3.89
	TiO <sub>2</sub>	0.93
	MnO	0.07
	$P_2O_5$	1.95
	CrO <sub>3</sub>	0.002

The solid residue (pyro-char) collected at the end of the pyrolysis process is composed of carbonaceous products (pyrochar) and ash which is a mixture of inorganic compounds. The pyro-char has a good Global Calorific Value (GCV = 12095 KJ/kg), a high amount of ash (44.86 %) and a low moisture rate (0.68 %) and sulfur (0.4 %). Thus, the analysis of pyro-char proves that this material is an energy carrier and could be used as a fuel in factories. Whereas, the high quantity of ash which contains hazardous compounds (heavy metal oxides) may decrease the heat value of the pyro-char and make its use as combustible unsafe for environmental health. Thus, many uses for pyro-char were planed and studied as shown below:

### Incorporation of pyro-char in bituminous formulation

Pyro-char samples were sent to a specialized laboratory in order to determine the particle size distribution (Figure 7). All particles had a size lesser than 20 mm and fifty percent of them were greater than 6.3 mm. Pyro-char was incorporated with rate (10%) in a comparable formulation of asphalt roadway for paving operations; composition is reported in the table 4. Appropriated tests were done according to international standards and reported with results in table 5.

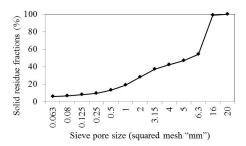


Figure 7 Granulometry of the pyrolytic solid residue

### Table 4 Composition of asphalt for roadway

Composition	Size (mm)	%
Pyro-char	0 - 2	10
sand	0 - 4	27
Gravel	4 - 6.3	10
Gravel	6.3 - 10	25
Gravel	10 - 14	21
Filler		2
Bitumen		5

roadway			
Test Methods	Characteristic	Results	Evaluation
NF EN 12697-31	void content to 10 gyrations in %	14.7	OK
NF EN 12697-31	void content to 10 gyrations in %	5.8	OK
NF EN 12697-12	r / R ratio in% (r after immersion / R dry)	82.2	OK
NF EN 12697-22	rut depth in % after 30,000 cycles	4.3	OK
NF EN 12697-26	Modulus at 15 ° C 10 Hz	11900	OK
NF EN 12697- 24+A1	Relative deformation in µdef at 10 <sup>6</sup> cycles, 10 ° C, 25Hz	135	ОК

The examination of results collected from the tests indicated that the prepared samples of asphalt for roadway in which 10 % of pyro-char was incorporated have a close similarity to the standard formula and gave a consistent product (Table 5); conclusion was reported by the specialized French laboratory.

## Energy carrier or feedstock in chemical industry

The use of pyro-char as energy carrier or feedstock in chemical industry requires a preliminary treatment. The proposed treatment process of pyro-char was done in a mixer with distilled water. The mixture was shacked vigorously and left to settle down for one hour. After decantation, a carbonaceous fraction floating on the surface was collected and dried. A residual solid fraction (ash) was collected from the bottom, should be composed of compounds such minerals, oxides, insoluble salts, etc...and eventual pollutants. The efficiency of proposed treatment mode is reported in the below table 6.

 Table 6 Characteristics of the formulation studied

Parameter	Gross Heat Value (KJ/kg)	Ash %	Efficiency %
Pyro-char	12094.7	45	31
Charcoal	20071	31	31
Ash for disposal		69	

The comparison of the heat value of the pyro-char before and after treatment indicated that the treatment of the solid residue leads to a very interesting carbonaceous products (charcoal) with a higher calorific value than that of the coal, lower rate of sulfur and ash. With a remaining ash rate 31 %, the purification process must be improved. This charcoal can be used as feedstock in chemical industry or in relatively safe mode as energy carrier and good fuel in cement factories for example. The remaining residual solid fraction (ash) is composed of minerals, oxides, insoluble salts, eventual pollutants, etc...

## Disposal in sanitary landfill

Another option to be taken in consideration is the safe landfilling of residual materials (ash). The rate of ash disposal was estimated in both cases before and after treatment of pyrochar; the mode of sorting giving sample B was admitted. In this sample, the average rate of rejects treated thermally at 300 °C was 20 %, leading to the formation of pyro-char (26 %) (Figure 4). Thus, if the direct disposal of pyro-char in sanitary landfill without treatment was chosen, the discharged residues represent around 5.2 % of the total mass of MSW feedstock. Whereas, if the pyro-char was treated and used as charcoal, the rate of residual ash obtained after burning represents 69 % of the hall pyro-char (table 6) and the disposed ash forms 3.6 % of the total mass of MSW feedstock.

# CONCLUSION

Thermal Treatment of two categories of MSW samples was performed in a heated reactor at fixed heating rate and in oxygen free environment, at different temperatures (200, 250 and 350 °C). Catalysts and additives were introduced to improve the MSW conversion rate. The yield and composition of the obtained pyro-products were determined, their physiochemical parameters were studied and the conversion parameters were optimized to satisfy the specificity of developing countries and environmental regulations.

The optimized thermal treatment was defined as a soft pyrolysis which is a catalytic treatment at low temperature (around 300 °C), contrary to the conventional pyrolysis. The examination of pyro-products yields showed that their rates tend to shift from solid to liquid and gas along the process when temperature rises and the decomposition rate accelerates at temperature higher than 300 °C. Furthermore, the catalytic decomposition was more efficient when sodium hydroxide is added as catalyst, while no effect is noted with zeolite. The soft pyrolysis of MSW samples A gave 50 % of pyro-water, indicating clearly that the thermal treatment of MSW with high content of vegetables (food waste) was not the convenient method of treatment, even if a previous drying process was applied. In fact, a supplement investment and operational cost were required for the post treatment of the huge amount of generated pyro-water. Thus, sorting and composting processes of organic materials must be applied before the soft pyrolysis of the MSW collected from rural areas (60-75% food waste).

Before treatment, the analysis of pyro-char showed a carbon rich mixture containing a high content of inorganic compounds (45%) including eventual pollutants (salts, heavy metals,..). This pyro-product can be incorporated in the asphalt roadway composition (ratio 1/10), leading to zero waste to be disposed. Moreover, it can be used as a carbonaceous energy carrier char similar to the coal (calorific value = 20071 KJ/Kg) or feedstock in chemical industry after the removal of mineral compounds (salts, silicates, carbonates heavy metals oxides, sulfur compounds,...) by physical separation in water bath. These toxic mineral compounds can be used either in the bitumen industry and cements or sent to sanitary landfill.

The obtained pyro-oil was chemically complex, composed of a mixture of different hydrocarbons, with an increasing viscosity along the pyrolysis process. Pyro-oil was free of water, characterized by a high calorific value and a low concentration of pollutants, making it a good fuel for internal use as well as for external.

Sodium hydroxide or calcium hydroxide (1 %) and calcium carbonate (2 %) must be added to the reactor in order to raise the pH of pyro-water from 3.9 to 6.7, to protect the pyrolysis system against corrosion and to optimize the operating conditions. Pyro-water was treated by ferric chloride at pH 8-9

to remove the dissolved organic compounds before being discharged safely in the sea.

The pyro-gas which is the non-condensable fraction at room temperature, known as a mixture of hydrogen, methane, carbon monoxide and low volatile hydrocarbons (syngas). It is free of dangerous products and can be used as an inner fuel in the reactor.

Soft pyrolysis had several advantages comparing to other thermal catalytic processes including a minimized volume of solid residue, generation of valuable products (char and oil) and the absence of poisonous emissions or chlorinated compounds (neutralized or trapped in the solid residue) which are released by direct incineration, gasification and conventional pyrolysis. Moreover, the control of emissions is easier due to the use of a low temperature and the release of a small volume of gaseous leading to reduce the investment and operating costs.

Finally, based on experimental results, environmental regulations and the most effective cost, complementary treatment procedures for sustainable management of MSW can be defined as an Advanced Combined Technologies (ACT – SCP), composed of three complementary steps in triangle: (i) Sorting lines to remove recyclable waste and food waste, (ii) Composting process to convert food waste to fertilizers and (iii) Soft pyrolysis to generate valuable products from all remaining rejects described in the following flow chart (Figure 8).

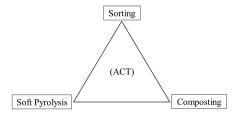


Figure 8 Flow chart of the Advanced Combined Technology (ACT-SCP).

(ACT-SCP) can offer many benefits over the other technologies: valuable products (pyro-oil and pyro-char), zero waste to be disposed, low cost treatment and environmental friendly technic. It was concluded that these processes represent the convenient methods to solve the acute Lebanese problem in managing the MSW and constitutes a model of management for developing countries.

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