

Recovery of Pyro-products obtained from the thermal treatment of Solid Municipal Waste by soft pyrolysis process

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Abstract—Soft pyrolysis was defined as a thermal treatment by which biomass is transformed under specific conditions to solid, liquid and gaseous fractions called pyro-products. Soft pyrolysis is one step of combined technologies in triangular shape (Sorting-composting-Soft pyrolysis) set to manage the acute problem of municipal solid waste and must leading to the status of zero waste. Soft pyrolysis has the role to treat thermally the residual waste collected from previous steps, sorting and composting in safe conditions in a relatively low temperature (300°C) in oxygen free environment and in the presence of chemical additives. The recovery of pyro-products is essential to reach the target of zero waste. In fact, after their characterization, different methods of treatment were tested and defined. Pyro-oil was treated by esterification and by dissolution in diesel oil cancelling deficiencies. The treated oil showed good characteristics such as calorific value (39000 kJ/kg), flash point (higher than 100°C and very low rate of pollutants such as sulfur (0.033ppm) or metallic traces), and then can be used as fuel in internal as well as external purposes in safe conditions. The recovery of solid residue was also studied. In specialized laboratories, the solid residue was incorporated (10%) in the formulation of asphaltene for paving roads and was tested successfully. On the other hand, solid residue was treated by fresh water. The carbonaceous fraction was analyzed and many final uses were determined such as solid fuel, as filler in rubber industry, thanks to its homogenous size distribution or as activated charcoal with excellent properties of adsorption for metallic ions and organic compounds. The gaseous fraction (synthetic gas) in small rate and dangerous pollutants free is directed for internal use as fuel. Finally, the wastewater generated was treated and several methods (chemicals, and photochemical) were applied. The photocatalytic decomposition by Ultra Violet radiation in the presence of titanium oxide and activated charcoal was the best means to reach the highest purity of water allowing its recycling or its reject in the nature with respect of environmental regulations.

Keywords—Soft pyrolysis; MSW; treatment; Recovery; Photocatalytic; Activation

I. INTRODUCTION

Municipal solid waste (MSW) is a major problem for most countries ^[1]. MSW is defined as organic and inorganic waste, produced by various activities of society and generated from several sources which have lost their value. Due to economic development and population growth, the generation of solid waste is increasing in volume and its nature is becoming more varied and more complex ^[2, 3].

The management of municipal solid waste is one of the major challenges facing authorities today ^[3, 4], particularly in Lebanon ^[5,6]. Solid waste management can be defined as all activities such as: collection, sorting, recycling and treatment ^[7]. The treatment of MSW involves different techniques: biological (anaerobic and aerobic) ^[8,9] and thermal (gasification, incineration and pyrolysis) ^[10,11]. Recently, with the increasing need for energy, several heat treatment processes have taken more interest ^[12, 13, 14]. However, the costs of air pollution control techniques required for heat treatment are generally very high because of the higher volume of fumes ^[6, 15].

In a previous work, an alternative and suitable technology was developed to manage municipal solid waste (MSW) in Lebanon and developing countries, in order to reach zero waste disposals ^[16]. This technology was defined as a combined technology based on three complementary processes in triangular shape (Sorting of recyclable materials and food waste - Composting of food waste and vegetables - Soft pyrolysis of the remaining residues), satisfying the specificity of developing countries such as limited resources and high content of vegetables (60-70%) with respect of the environmental restrictions. MSW was then, converted into valuable products (recyclable materials, compost, char, oil), with zero waste disposal. This technology could be the convenient treatment method to solve the acute Lebanese problem of MSW management and may establish a model of management for developing countries.

In fact, interesting conditions to thermally treat the residual waste were optimized and named as soft pyrolysis^[16]. They are an oxygen free environment, at a heating rate of $2.5\text{ }^{\circ}\text{C min}^{-1}$ during six hours. Compared to conventional pyrolysis^[17,18,19], it is characterized by a lower disintegration temperature ($300\text{-}350^{\circ}\text{C}$) and the nature of chemical additives^[17] such as sodium hydroxide (1%) as a catalyst and Calcium carbonate (2%). Under such conditions, the yields of pyro-water, tar and char were 14%, 33.6%, and 26%, respectively. These yields are strongly related to the operating conditions, particularly the temperature and the composition of MSW at sources. Furthermore, as conventional pyrolysis^[17], soft pyrolysis reduces strongly the volume of MSW whereas the nature and composition of gas flux are better controlled^[16]. In fact, the volume of gas flux is reduced; the poisonous gases are neutralized by the additives and the formation of dangerous compounds such dioxins or furans are inhibited. Moreover, heavy metals and inorganic salts are trapped in solid phase, emissions are easily controlled and operating and maintenance costs are greatly reduced.

The physicochemical properties of pyro-products showed potential valuable products which need treatment before use^[16]. Pyro-char is a black solid residue obtained by the pyrolysis of organic materials. Its properties and yield are affected by the nature of parent feedstock and by the applied operating conditions^[15]. The analysis of pyro-char showed a carbon rich mixture (55%) with a high content of ash (45%), including eventually some pollutants (salts, heavy metals,)^[16]. The disposal of char fraction may represent an easy option, whereas it is a wasting mode of valuable product. Moreover, since the recent environmental restrictions, char recovery represents a great deal in order to develop environmental friendly technologies.

Untreated pyro-char has been tested successfully for its incorporation in asphalt roadway for paving operation under a fractional ratio 1/10^[16]. Analysis showed pyro-oil as a chemically complex product, composed of a mixture of different hydrocarbons characterized by a high calorific value ($39\ 000\ \text{kJ/Kg}$)^[20], but its viscosity will increase and flash point will be too low (30°C), making its direct use unsafe^[16]. Moreover, the generated wastewater (pyro-water) was analyzed, containing organic and non-organic pollutants. Non-condensable fraction (syngas) in small rate, volatile hydrocarbons can be used directly as an inner fuel in the reactor.

2. METHODOLOGY

2.1. Samples Preparation

MSW samples were collected from municipal garbage and sorted giving approximately 20% of recyclable materials (hazardous electronic wastes, and batteries), 60% of food waste and vegetables, and 20 % of residual solids. These, later on, were shredded and homogenized in order to be treated thermally.

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 a controlled heater equipped with thermocouple (Mantle Heater), and the thermal conversion was performed at a relatively low temperature, normal pressure and oxygen free environment.

Five hundred grams of the MSW sample were introduced into the reactor containing 5 g of the Catalyst (sodium hydroxide) and 10 g of additives (calcium carbonate or calcium hydroxide). The heating was then initiated at a rate of $2.5\text{ }^{\circ}\text{C min}^{-1}$ to reach the preset temperature around $300\text{ }^{\circ}\text{C}$ and kept under 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 $100\text{ }^{\circ}\text{C}$. 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 (Scrubber). 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 or tar and (ii) an aqueous fraction called pyro-water. These fractions were stored in glass bottles in order to be characterized and to undergo later an appropriate treatment (Fig.1). At the end, the metallic reactor was allowed to cool down; a solid residue (pyro-char) was then removed and stored for analysis (Fig.1). The transformation rates of the organic materials are illustrated in table 1.

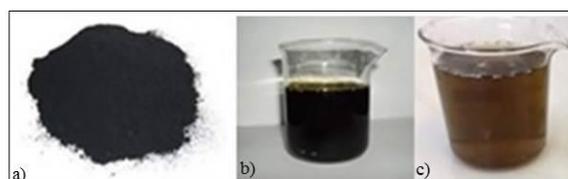


Fig. 1. Fractions of pyro-products: a) oil fraction, b) aqueous fraction, c) solid fraction

TABLE 1. Rate of pyro-products.

Rate	Pyro-products			
	water	Oil	Charcoal	Gas
Percentage	11	28	36	25

2.2. Treatment of Pyro-products

2.2.1. Treatment of the Pyro-water

The treatment of pyro-water has been performed following the below methods:

1- With Ferric chloride: 50 mL of pyro-water were treated with ferric chloride (FeCl_3) as flocculent. The solution was buffered at pH 9 using sodium hydroxide, stirred to allow flocculation and flocs were then left to

settle down. The precipitate was removed by filtration using filter paper (0.45 μm as porosity), and the filtrate was analyzed (Fig. 2b).

2- Fenton reagents: 1 mL of H_2O_2 is added to 50 mL of pyro-water. The pH is adjusted to 3-4 by adding one drop of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and two drops of polyelectrolyte (for better separation). The mixture was then left at rest for 30 minutes. A separable precipitate was formed and treated water was collected for analysis (Fig. 2c).

3- Combined treatment (FeCl_3 /Fenton): Pyro-water was first treated with FeCl_3 (part 1). The obtained filtrate was then treated by the Fenton process as showed in part 2 and at the end the filtrate is separated for analysis (Fig. 2d).

4- Photocatalytic Treatment: The treatment of water polluted by heterogeneous photocatalysis in the presence (TiO_2) is carried out using the most energetic part of the solar spectrum ($\lambda < 300 \text{ nm}$) in order to induce oxidation-reduction reactions.

The effects of several parameters were studied on a sample of 50 ml of polluted water, among which the titanium oxide content (0.05- 0.1- 0.2 - 0.4g), the irradiation time (10 till 90 min) and the presence of activated charcoal (Fig. 2).

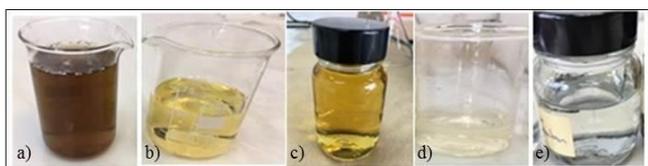


Fig. 2. Pyro-water before treatment (a), treated with FeCl_3 (b), with Fenton(c), combined (d), photocatalytic treatment (e).

2.2.2. Treatment of the Pyro-oil

The treatment of pyro-oil was performed using two methods:

1-Esterification: It is carried out by mixing a mass of pyro-oil with ethanol in a rate 4:1. The phosphoric acid is added as catalyst and the mixture is heated under reflux during one hour. Fractional distillation was done at 300-350°C. A distillate with two phases are formed and separated by density to aqueous and oily fractions. The oily fraction was analyzed, while the aqueous fraction was added to pyro-water (table 2).

2- Dissolution in petroleum diesel oil: Pyro-oil samples were mixed with an equivalent volume of petroleum diesel oil in order to improve the properties (reduction of viscosity, increase the flash point,..). After stirring and resting (15mn), a solid residue was formed at the bottom flask. After filtration, the liquid phase is separated into aqueous and oily fractions (table 2). The oil fraction was later analyzed, while the aqueous fraction was added to pyro-water.

TABLE 2. Composition of oily fraction after treatment.

Treatment mode	Fraction Rate (%)		
	Oily	Aqueous	Solid residue
Esterification	34	18	48
Dissolution	44	26	30

2.2.3. Treatment of the Pyro-charcoal

The treatment of charcoal was performed by washing in fresh water. After stirring and resting, the carbonaceous fraction floats at the surface of water and then was collected to be dried, whereas, a second fraction settled down. It is composed of insoluble salts including potential pollutants. Another fraction was found to be soluble in water. The collected wastewater was added to pyro-water for treatment. The table 3 illustrates the percentage of each fraction obtained after treatment by distilled water.

2.2.4. Preparation of Activated Charcoal

To an 8 g sample of carbonaceous fraction, 12 ml of concentrated sulfuric acid were added. The mixture was stirred and heated at 170°C during 30 min. The pH was adjusted by dilution to 6-7. The activation of the charcoal was completed by the addition of 16 ml ethanolamine. The solid phase was separated and dried in an oven at 110°C during 2 hours. The prepared sample was characterized and its performance for the adsorption of metals and organic compounds was successfully tested.

2.3. Physicochemical Analysis of Pyro-products

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™ instrument. The concentrations of dissolved elements were determined by an Atomic absorption spectrophotometer (Perkin-Elmer PinAAcle 900T AAS) and ionic chromatography (ThermoFisher Scientific). Dissolved anions (sulfate, nitrite, nitrate, phosphate, and chloride, metallic ions,...) 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. In addition, the chemical composition of the oil fraction was analyzed by gas chromatography coupled with mass spectrometry (Shimadzu, GCMS-TQ8050.). Spectroscopic analyzes by IR, XR and SEM was carried out as well as by particle size analysis of the treated pyro-coal samples. Specific analysis was carried out in specialized laboratories (Asphalt, charcoal,...).

TABLE 3. Composition of charcoal after treatment.

Treatment mode	Fraction Rate (%)	
	Carbonaceous	Settleable and dissolved
Distilled water	25	75

3. RESULTS AND DISCUSSIONS

The physicochemical characterization of pyro-products was carried out before and after treatment in order to follow the evolution of their properties and to assess properly their recovery, respecting the environmental regulations and economic requirements.

3.1. Characterization and Recovery of Pyro-charcoal Samples

3.1.1. Characterization of Pyro-charcoal Samples

The efficiency of pyro-charcoal treatment was evaluated through the physicochemical and spectroscopic speciation. Table 4 reports the physicochemical characteristics of the pyro-charcoal samples before and after treatment.

The analysis shows that the ash in the non-treated sample with rate 40.03% has the following chemical composition (table 5).

Moreover, The spectroscopic characterization of pyro-charcoal was carried out by IR spectroscopy for all charcoal samples (Fig. 3).

The IR spectra showed that the three analyzed samples have the same peaks distribution. Thus, the washing of charcoal by water doesn't modify its chemical composition. Whereas, the activated charcoal has additional peak observed at 2400 cm^{-1} , corresponding to the added cyanide group. This result is comparable to the reference sample. However, this former showed an additional moderate peak (1000 cm^{-1}) for a phosphate group which is not observed in the prepared activated charcoal.

TABLE 4. Physical and chemical properties of the pyro-charcoal.

Parameter	Results		
	Before treatment	After treatment	Coal (reference)
Total humidity (%)	5.25	6.27	8 à 20
Sulfur (dry sample) (%)	0.21	0.21	< 2
Ash (dry sample) (%)	40.03	36.23	> 12
Sulfur (ash) (%)	0.39	0.45	----
Gross Calorific Value (kj/kg)	3082	3348	5800-8000
Net Calorific Value (kj/kg)	3253	3572	5800-8000

The effect of treatment on the particle size distribution of charcoal samples was studied. The particle size distribution of non-treated charcoal samples showed

that fine particles ($< 100\text{ }\mu\text{m}$) represent 57% of the whole sample (Fig 4a), whereas it rise to reach 88% for treated sample (Fig. 4b). Thus, the treatment of pyro-charcoal increases the percent of fine particles by 31% and gives a more homogeneous product.

TABLE 5. Chemical composition of the pyro-charcoal.

Parameter	Results (%)
SiO ₂	22.60
Al ₂ O ₃	4.70
Fe ₂ O ₃	3.77
CaO	52.98
MgO	2.18
SO ₃	2.07
K ₂ O	1.53
Na ₂ O	3.89
TiO ₂	0.93
MnO	0.07
P ₂ O ₅	1.95
CrO ₃	0.002

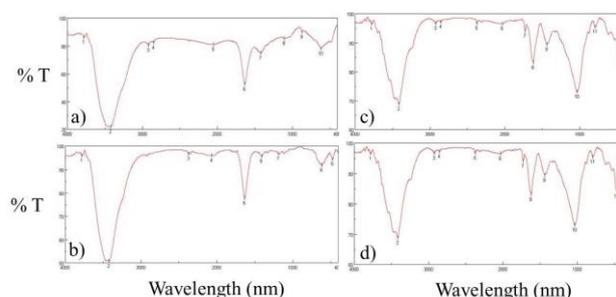


Fig. 3. IR spectra of: (a) non-treated samples, (b) treated samples, (c) prepared activated charcoal, (d) activated carbon as reference.

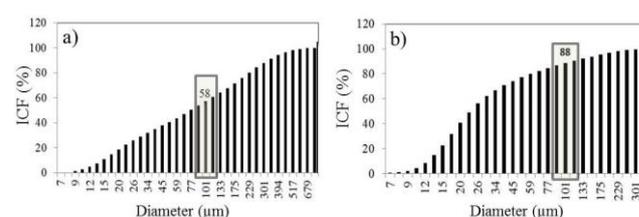


Fig. 4. Size distribution of original pyro-char sample (a), treated sample (b).

3.1.2. Recovery of Charcoal:

3.1.2.1. Incorporation of Pyro-charcoal in Bituminous Formulation (Non-treated)

In a previous work reported by Khalil [16], showing that untreated charcoal can be incorporated in the composition of asphalt for roads paving. The addition of 10% of charcoal to the asphalt leads to a consistent end product closely similar to the standard formula (tables 6 and 7).

TABLE 6. Formulation of asphalt for road paving.

Composition	Size (mm)	Percentage
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

TABLE 7. Characteristics of the prepared asphalt for 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 % 30,000 cycles	4.3	OK
NF EN 12697-26	Modulus at 15°C 10Hz	11900	OK
NF EN 12697-24+A1	Relative deformation in μ def at 10^6 cycles, 10°C 25 Hz	135	OK

3.1.2.2. Disposal in Sanitary Landfill

Another option to be taken in consideration is the sanitary landfilling of pyro-charcoal (ash). The rate of ash to be disposed was estimated to be less than 5.2% of the initial MSW feedstock if the pyro-charcoal is not treated, whereas it is less than 3.6% in case of treatment.

3.1.2.3. Source of Energy (treated)

Results reported in table 3 indicate that after washing the net caloric value of charcoal has increased by 10%, whereas the quantity of released ash decreases significantly. Moreover, a low rate of sulfur and moisture were found, indicating that treated charcoal can be used safely as an energy carrier for factories fueling.

3.1.2.4. Filter for Metals Adsorption (activated charcoal)

After been activated the performance of charcoal to remove dissolved elements was studied. Thus, 0.2 g of activated charcoal was added into different solutions (200 ml) containing copper, iron or lead salts. The efficiency of the prepared activated charcoal is defined as the percentage of the adsorbed metal over its initial concentration. The examination of results illustrated in table 8 shows an excellent

capacity of adsorption in short time less than 25 min comparable to reference. With iron the efficiency reach almost 100% but decreases with higher initial concentration, whereas it is between 60-70% for copper and lead without change if the initial concentration increases. These results demonstrate the adsorption properties of the prepared activated charcoal used in treatment of wastewater and effluent gas.

TABLE 8. Performance of prepared activated charcoal.

Ions	Efficiency (%) versus time and concentration				
	Time (min)	Activated charcoal			Reference
		Concentration (ppm)			Concentration (ppm)
Fe ³⁺	0	4.30	6.97	26.76	26.76
	25	0.07	0.67	13.97	12.86
	90	0.01	0.28	12.88	11.88
	Efficiency	99	96	52	55
Cu ²⁺	0	5.79	6.31	38.76	38.76
	25	3.42	3.76	25.56	27.38
	90	2.79	3.52	16.23	21.24
	Efficiency	52	50	58	45
Pb ²⁺	0	-	53	165	165
	30	-	17	50	46
	Efficiency	-	67	72	73

Moreover, the adsorption of dissolved ions by the prepared charcoal was studied with treated water. To 50 ml of the water samples, 0.05 mg of activated charcoal is added in the same conditions. The results reported in the table 9 improve significantly the quality of water and confirm the performance of prepared activated charcoal.

TABLE 9. Efficiency of treatment by activated charcoal.

Parameter (ppm)	Efficiency of treatment		
	Before	After	(%)
Copper	2.75	0	100
Iron	49	0	100
Zinc	3.5	0.14	96
Lead	2	0.1	95
Nitrites	0.1	0	----
Chlorides	1	0	----

3.1.2.5. Chemical Feedstock

The particle size distribution of treated pyro-charcoal with less than 100 μ m, allows its use as filler in rubber industry, which requires homogeneous distribution in size.

3.2. Characterization and Recovery of Pyro-oil

3.2.1. Characterization of Pyro-oil

The analysis of pyro-oil indicated that it is composed of a mixture of hydrocarbons with different

physicochemical properties [16] reported in table 10. The treatment of pyro-oil show comparable performance of the obtained treated oil for both methods but with better yield for dissolution (Fig. 5). They improve significantly the properties of pyro-oil and cancel noticed deficiencies. The pyro-oil becomes less acidic (pH=5) with higher net calorific value (+7%), greater flash (75°C) and lower viscosity.

TABLE 10. Effect of treatment on the characteristics of pyro-oil.

Parameter	Pyro-oil		
	Before treatment	Treated by Esterification	Treated By Dissolution
Aspect	Dark brown	Dark brown	Dark brown
pH	3.28	5.23	5.6
Density	0.9097	0.8619	0.8623
Viscosity	> 7	2.9917	6.0940
Water & Sediment	0.6	0.05	1.5
Flash point(°C)	31	79	105
Gross Calorific Value (Mj/kg)	42.40	45.37	45.37
Net Calorific Value (Mj/kg)	39.80	42.61	42.61
Sulfur	0.033	0.032	0.02
Acid number (mg KOH/g)	140	32.46	63.21

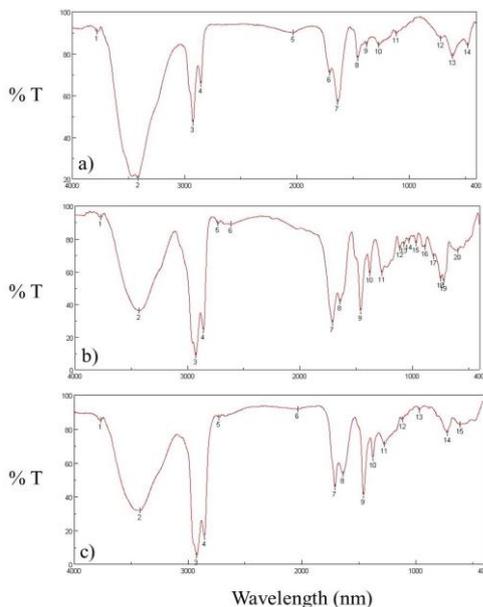


Fig. 5. IR characterization of pyro-oil: (a) before treatment, (b) treated by esterification, (c) treated by dissolution.

Furthermore, the efficiency of pyro-oil treated by esterification process was studied by NMR. The spectra of C and H are illustrated in Fig. 6. They confirm that the oil is a mixture composed of various

hydrocarbons (aliphatic chains, aromatics, alkenes, aldehydes, ketones, etc,...). In addition, the success of esterification process is confirmed by the absence of peaks at 10-12 related to acids.

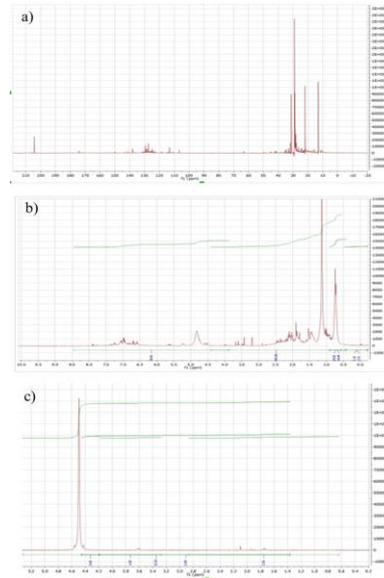


Fig. 6. X-rays characterization of pyro-oil: (a) C-RMN of organic fraction, (b) H-RMN of organic fraction, (c) H-RMN of aqueous fraction.

3.2.2. Recovery of Pyro-oil

The characterization of treated pyro-oil shows that it has good properties of fuel (table 10) such as calorific value (39000kj/kg) which is closer to that one of diesel oil (42000kj/kg) and low rate of sulfur (0,033 pm). With such properties, the pyro-oil can be used as fuel for internal as well as for external use.

3.3. Characterization of Pyro-water

The physical and chemical properties of pyro-water were determined [16], showing that pyro-water is polluted and need treatment (table 11).

TABLE 11. Properties of pyro-water before treatment.

Parameters	Results
Density at 15°c	1.04
pH	6.77
Conductivity(mS/cm)	9.38
Aspect	Dark brown
TOC (ppm)	131.74
Sodium (ppm)	0.6
Potassium (ppm)	0.6
Cadmium (ppm)	0
Iron (ppm)	14.14
Lead (ppm)	0
Calcium (ppm)	0.42
Zinc (ppm)	0.34
Copper (ppm)	0.019
Silicon (ppm)	0
Nitrates (ppm)	0
Nitrites(ppm)	0
Chlorides (ppm)	328

The efficiency of chemical and photocatalytic methods is evaluated by the rate of total organic compounds (TOC) and results are reported in tables 12 and 13, respectively.

The comparison of chemical treatment methods shows that the combination of treatment with FeCl_3 followed by the Fenton process is more efficient. The color of the pyro-water shifts from dark brown to light yellow after treatment by FeCl_3 and Fenton reaction. Whereas, it becomes transparent after been treated by combined method and the concentration of the total organic carbon decreases to reach 67.87 ppm while the rate of TOC still high.

The photocatalytic treatment of pyro-water was studied versus the rate of titanium oxide by analyzing the TOC of treated water versus time of irradiation (Fig.7).

The photocatalytic treatment shows a better performance (80%) than the chemical process after 10 min only of radiation using 0.1 g of $\text{TiO}_2/50\text{ml}$. In addition to its capacity of adsorption for metallic ions (table 9), the presence of activated charcoal appeared to be beneficial for adsorption of organic compounds also. The reduction of TOC reaches (94%) and water became completely transparent, and the recycling of treated water is possible with respect to environmental regulations.

TABLE 12. Efficiency of chemical methods for the treatment of pyro-water.

Parameter	Efficiency of Treatment			
	Before	Treatment mode		
		FeCl_3	Fenton	Combined
Aspect	Dark brown	Light yellow	Light yellow	Transparent
TOC (ppm)	131.74	95.96	99.34	67.87

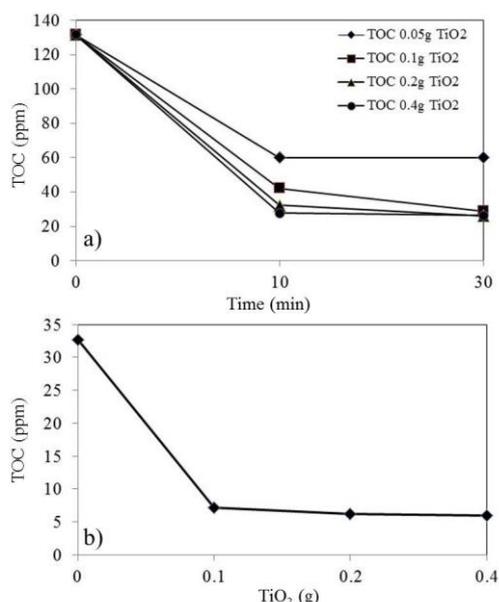


Fig. 7. Effect of TiO_2 rate on the variation of the total organic carbon (TOC).

TABLE 13. Efficiency of photocatalytic treatment of pyro-water.

Parameter	Efficiency of treatment		
	Before	Photocatalytic	Photocatalytic + Activated charcoal
Aspect	Dark Yellow	Light Yellow	Transparent
TOC (ppm)	131.7	26.2	9.1

4. CONCLUSION

Thermal Treatment of residual waste was performed under soft-pyrolytic conditions. In previous work, soft pyrolysis was one of three processes in triangular steps forming the advanced technologies for the treatment of MSW: (i) Sorting lines to remove recyclable waste and food waste, (ii) Composting process to convert food waste to fertilizers and (iii) Soft pyrolysis of residual waste to generate valuable products.

Soft pyrolysis was defined as a thermal catalytic treatment at low temperature (around 300°C), an oxygen free environment, and a heating rate of $2.5^\circ\text{C min}^{-1}$ during six hours and in the presence of sodium hydroxide (1%) and Calcium carbonate (2%) as additives. 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. Under soft pyrolysis conditions, yields of pyro-products are 14%, 33.6% and 26 % for pyro-water, pyro-oil and pyro-char, respectively.

The analysis of raw pyro-char showed a carbon rich mixture containing a high amount of inorganic compounds (45%) including pollutants such as heavy metals salts. This pyro-product can be incorporated in the asphalt roadway composition (ratio 1/10) with respect of standard formulation, leading to zero waste disposal. However, the raw pyro-char can be treated by washing in water to give more valuable products. The obtained charcoal is the carbonaceous fraction with high net calorific value (3572 KJ/Kg), can be used as safe solid fuel. Furthermore, the homogeneous size particles of the treated pyro-charcoal allow its incorporation in rubber industry as filler. On the other hand, the activation of treated charcoal gives a product with excellent adsorption properties either for organic compounds or metallic ions. The residual solid fraction can be either used in the bitumen industry, cement industry or sent to sanitary landfill in safe conditions.

The obtained pyro-oil was chemically complex, composed of a mixture of different hydrocarbons. Its physicochemical properties were improved after treatment either by esterification or dissolution in petroleum diesel. The flash point was increased from 31°C to higher than 80°C , the acidity was reduced and the viscosity was lowered. Thus, the treated oil,

characterized by a high calorific value and a low concentration of pollutants, is considered as a good fuel for internal as well as for external use.

The organic and non-organic pollutants in pyro-water are eliminated by chemical and photocatalytic methods. The highest depollution efficiency was obtained using a combined treatment between the photocatalytic process and the activated charcoal. The depolluted water satisfies the environmental regulations and can be discharged safely in surface water.

The released pyro-gas, defined as the non-condensable fraction at room temperature, is composed of a mixture of hydrogen, methane, carbon monoxide and low volatile hydrocarbons (syngas) can be used as inner fuel in the reactor.

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