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Syntheses and Modelling of the Activated Carbon Made by Olive Cake Residues by Pyrolysis and Actived by a Water Vapour Current at One Process

[1]Fethi Nebili and [2]Faouzi Bouachir
[1]Department of Industrial Chemicals, INSAT,
[2]University of Carthage, National Institute of Sciences Applied and Technology (INSAT),
Street of the Earth, Northern Urban Centre BP 676-1080, Tunis-Cedex, Tunisia

Abstract: Now-a-days, it is indispensable to contribute to the durable development by using a local biomass and more particularly to the valorisation of the olive cake residue to carry out a raw local autonomy material, a clean process, saving in atoms and energy autonomy. Within this framework and considering the availability of the olive cake residue in Tunisia and the absence of its thermochemical valorisation (pyrolysis, gasification and combustion), researchers were interested in this research in the study of slow pyrolysis between 500 and 800°C of this biomass and its activation in only one stage in automatic and programmable oval furnace. The furnace is equipped with a sample door out of stainless of cylindrical form tight in a water vapour current. The choice of the activation method is guided by the preoccupation with a simple process development of application. The study of the productivity of the method indicated reveals a significant output. The products obtained are characterized by specific microspores surfaces S_{mi} between 400 and 800 $m^2 g^{-1}$. The technique of the experimental design helps us to optimize the process and to minimize the numbers of the tests. The increasing request of the activated carbons, however relates to the field of water and the environment.

Key words: Olive cake residue, pyrolysis, thermochemical activated carbon and life cycle assessment, experimental design, water vapour, framework

INTRODUCTION

Preparation of active carbon: The carbon made by olive cake residues relyson traditional slow pyrolysis and actived by a water vapour current at one process (Benabdaah *et al*., 1994; Minkova *et al*., 2001; Nefzaoui, 1999).

Several tests were accomplished by the introduction of 40 g quantity of olive cake residue in a programmable automatic oval furnace. The furnace is equipped with a cylindrical stainless sample door. Of this door, the water vapour enters with adjustable flow between 0.5 and 1 L h^{-1} and exits the exhaust fumes. Both of them were heated at the desirable temperature of 500-800°C. The speed of heating used is between 5 and 10°C mn^{-1}. Researchers use this average until reaching the stage of activation. The final temperature rest in duration between 5 and 30 mn. At the end of the reaction, the heating is stopped and the cooling of the furnace is accomplished under the same water vapour current.

The samples of the activated carbon should be crushed abd filtered to 80 μm. They should be driing oven at 120°C during 24 h. Desiccators should realize their cooling.

Analyses Carbon Hydrogen Nitrogenises (CHN): Elementary analysis CHN of olive cake residue and activated carbon obtained by pyrolysis at various temperatures, gives various composition as C, H, O and N as the following anhydrous weight (Table 1).

Ability of adsorption of nitrogen by ATD-ATG: The activated carbon are dried and degassed to 150°C during 30 mn under a 10^{-4} Torr vacuum at 25°C. The phase of nitrogen adsorption is accomplished at ambient temperature until the saturation point. Although, these measurements did not allow to determine the specific surface of the samples, they are useful for a relative classification of the capacities of adsorption. These properties are in relation with specific surfaces of the activated carbon. The results obtained are mentioned in Table 2.

Table 1: Ultimate analysis CHN of activated carbon

T_p (°C)	C (%)	H (%)	N (%)	Ash (%)	O_2 (%)
Olive cake residue	48.1	6.4	3.2	4.1	38.2
500	85.7	4.1	-	1.5	8.7
600	89.3	2.8	-	1.7	6.2
700	92.1	1.9	-	2.1	3.9
800	93.5	1.5	-	2.9	2.1

Corresponding Author: Fethi Nebili, Department of Industrial Chemicals, INSAT, Street of the Earth, Northern Urban Centre BP 676-1080, Tunis-Cedex, Tunisia

Table 2: Experimental results

Parameters	Results: S_{mi} langmuir ($m^2 g^{-1}$)	S_{mi} BET ($m^2 g^{-1}$)	S_{mi} burn-off ($m^2 g^{-1}$)	W_o burn-off ($cm^3 g^{-1}$)	ρ_{mh} (%) wet cake	ρ_{ms} (%) dry cake	N_2 adsorbed ($cm^3 g^{-1}$)	C_6H_6 adsorbed ($cm^3 g^{-1}$)	I_2 adsorbed ($cm^3 g^{-1}$)	$C_{16}H_{18}ClN_3S$ adsorbed ($cm^3 g^{-1}$)	C (%)
Influence of the final temperature of pyrolysis T_p: Q = 0.75 L h^{-1}, V = 5°C mn^{-1} and t = 20 mn											
500 (°C)	531	449	525-665	0.499	41.85	45.00	1.623	0.158	0.097	0.105	85.7
600 (°C)	640	544	611-774	0.581	28.25	30.37	6.073	0.240	0.127	0.168	89.3
700 (°C)	708	600	641-811	0.609	23.57	25.34	12.705	0.303	0.146	0.254	92.1
800 (°C)	749	636	667-845	0.634	19.35	20.80	17.166	0.329	0.157	0.298	93.5
Influence of the duration of carbonization t: Q = 0.75 L h^{-1}, V = 5°C mn^{-1} and T_p = 700°C											
5 (mn)	686	586	634-803	0.602	24.60	26.45	12.310	0.294	0.141	0.246	91.8
10 (mn)	693	590	638-808	0.606	23.95	25.75	12.436	0.297	0.143	0.249	91.9
20 (mn)	708	600	641-811	0.609	23.57	25.34	12.705	0.303	0.146	0.254	92.1
30 (mn)	712	605	644-816	0.612	23.06	24.80	12.777	0.305	0.147	0.255	92.2
Influence of the heating speed of the furnace V: Q = 0.75 L h^{-1}, T_p = 700°C and t = 20 mn											
(5 °C mn^{-1})	708	600	641-811	0.609	23.57	25.34	12.705	0.303	0.146	0.254	92.1
(10 °C mn^{-1})	661	562	629-796	0.597	25.44	27.35	11.862	0.283	0.136	0.237	90.4
Influence of the water vapour flow Q: T_p = 700°C, V = 5°C mn^{-1} and t = 20 mn											
0.5 (L h^{-1})	641	492	644-816	0.612	22.98	24.71	11.503	0.274	0.132	0.230	90.3
0.75 (L h^{-1})	708	600	641-811	0.609	23.57	25.34	12.705	0.303	0.146	0.254	92.1
1.00 (L h^{-1})	711	603	641-812	0.609	23.48	25.25	12.759	0.304	0.147	0.255	92.1

Adsorptions by fourier transform infrared spectroscopy: FTIR is the method that researchers had for the quantitative determination of the adsorbents benzene, methylene blue and iodine at 25°C and P_{atm}.

The activated carbons are immersed in a quantity of ethanol solution containing adsorbed with a given concentration. The difference between the initial and final concentrations is representative for the adsorbed quantity. The measurement was made by the method that the adsorbed final quantity was put in the horizontal part of the asymptote adsorption isotherm.

The mixture of the activated carbon-solution of adsorbent was put in a thermostatic bath at 25°C and agitated during 30 mn. The activated carbon solutions obtained by filtration after 24 h have undergo a quantitative analysis which uses FTIR. The experimental results are mentioned in Table 2.

BET and langmuir specific surface: The measurement of specific surfaces by the BET and langmuir methods were realized out under conditions which guarantees a total desorption of the surface of the samples (temperature of desorption 400-500°C). However, the results obtained reflect the tendency notes at the time of the determination of benzene, iodine and methylene blue index. The results obtained are mentioned in Table 2.

The product resulting from pyrolysis and the activation from the olive cake residue with 800°C present the best performance. The found value with 800°C testifies to a strong activation of the reaction of following formation of the pores: $C+H_2O \rightarrow CO+H_2$.

The temperature of carbonization is certainly the most significant factor which conditions the outputs and the physicochemical properties of carbon with constant water vapour flow.

RESULTS AND DISCUSSION

The normal working conditions are: Olive cake residue obtained by pressure of South Tunisian (humidity of olive cake residue = 7%, T_p = 700°C, Q = 0.75 L h^{-1}, V = 5°C mn^{-1} and t = 20 mn).

With constant pressure, the principal factors that influence the process of carbonization (output) and determine the quality of the product are:

- The heating speed of the furnace V (°C mn^{-1})
- The final temperature of pyrolysis T_p (°C)
- Water vapour flow Q (L h^{-1})

The adsorption of gases requires pores from 1-2 nm whereas pores from 2 nm are enough adsorption to the liquids.

Study of the experimental design: To constitute a planning strategy of experiment in order to obtain solid and adequate efficiently conditions and economically, a complete factorial design 2^3 is realized out to determine the factors and signify interactions that will frequently lead to an analysis and a relatively simple statistical interpretation of the results (Goupy and Creighton, 2009). The characterizations of the study and the experimental fields of the variable factors are, respectively defined in the experiment matrix following in Table 3-5 to study the effect of the various factors on the quality and the quantity of the activated carbon. Table 3 shows the whole of the experimental answers Y1-6 obtained under the influence of 3 factors (temperature of pyrolysis, heating speed and water vapour flow). The studied answers are mentioned in Table 5. One represents the matrix of the effects starting from the selected polynomial model for the plan 2^3.

Table 3: Matrix of experimental design for the activated carbon development

		Factors			Interactions				Reponses					
Tests	Means	A	B	C	AB	AC	BC	ABC	Y1	Y2	Y3	Y4	Y5	Y6
1	1	-1	-1	-1	1	1	1	-1	478	404	1.461	0.142	0.087	0.095
2	1	1	-1	-1	-1	-1	1	1	733	623	6.954	0.275	0.145	0.192
3	1	-1	1	-1	-1	1	-1	1	425	359	1.298	0.126	0.078	0.084
4	1	1	1	-1	1	-1	-1	-1	717	609	6.802	0.269	0.142	0.188
5	1	-1	-1	1	1	-1	-1	1	568	480	1.737	0.169	0.104	0.112
6	1	1	-1	1	-1	1	-1	-1	779	661	17.853	0.342	0.163	0.310
7	1	-1	1	1	-1	-1	1	-1	552	467	1.688	0.164	0.101	0.109
8	1	1	1	1	1	1	1	1	764	649	17.509	0.336	0.160	0.304

Table 4: Factors field

	A	B	C
Factors	pyrolysis temperature	heating speed	water vapour flow
Level (-1)	500°C	5°C min^{-1}	0.5 L h^{-1}
Level (+1)	800°C	10°C min^{-1}	1.0 L h^{-1}

Table 5: Experimental reponses

Reponses	Results	Units
Y1	S_{mi} Langmuir	$m^2 g^{-1}$
Y2	S_{mi} BET	$m^2 g^{-1}$
Y3	Nitrogen N_2 adsorbed at 25°C	$cm^3 g^{-1}$
Y4	Benzene adsorbed at 25°C and P_{atm}	$cm^3 g^{-1}$
Y5	Iodine adsorbed at 25°C and P_{atm}	$cm^3 g^{-1}$
Y6	Methylene blue adsorbed at 25°C and P_{atm}	$cm^3 g^{-1}$

Polynomial mathematical model: A complete factorial design 2^3 is realize to determine the significant mailmen and interactions. The factorial experimental designs use a polynomial mathematical model which connects the response y to x_1-x_3 (Goupy and Creighton, 2009):

$$y = a_0 + a_1.x_1 + a_2.x_2 + ... + a_n.x_n + \sum_{i,j=1i\neq j}^{n} a_{ij}.x_i.x_j + \sum_{i,j,k=1i\neq j\neq k}^{n} a_{ijk}.x_i x_j.x_k + ...$$

Where, a_0, a_1... is the coefficients of the polynomial. For a design with 3 factorial x_1-x_3 one obtains:

$$Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 + a_{123}x_1x_2x_3$$

The effect models were representing into the matrix (Table 3) is indicate in the equations later than:

$$Y1 = 101.333 + 0.753333x_1 - 42.3333x_2 + 132.667x_3 + 0.0486667x_1x_2 - 0.0533333x_1x_3 + 38.8x_2x_3 - 0.048x_1x_2x_3$$

$$Y2 = 78.3333 + 0.653333x_1 - 35.7333x_2 + 114.667x_3 + 0.0406667x_1x_2 - 0.0533333x_1x_3 + 32.8x_2x_3 - 0.04x_1x_2x_3$$

$$Y3 = 10.5403 - 0.0181567x_1 - 0.161067x_2 - 36.106x_3 + 0.000211333x_1x_2 + 0.07286x_1x_3 + 0.2496x_2x_3 - 0.000408x_1x_2x_3$$

Table 6: Comparison of the experimental and calculated results

T/V/Q	Results	Y1	Y2	Y3	Y4	Y5	Y6
500/5/0.75	Measured	531	449	1.623	0.158	0.097	0.105
	Calculated	523	442	1.599	0.155	0.096	0.103
600/5/0.75	Measured	640	544	6.073	0.240	0.127	0.168
	Calculated	601	509	5.200	0.206	0.115	0.153
700/5/0.75	Measured	708	600	12.705	0.303	0.146	0.254
	Calculated	678	575	8.802	0.257	0.135	0.202
800/5/0.75	Measured	749	636	17.166	0.329	0.157	0.298
	Calculated	756	642	12.403	0.308	0.154	0.251
700/5/0.5	Measured	641	492	11.503	0.274	0.132	0.230
	Calculated	648	550	5.123	0.231	0.126	0.160
700/5/1	Measured	711	603	12.759	0.304	0.147	0.255
	Calculated	709	601	12.481	0.284	0.143	0.244
700/10/0.75	Measured	661	562	11.862	0.283	0.136	0.237
	Calculated	657	557	8.601	0.250	0.131	0.196

$$Y4 = 0.022 + 0.00024x_1 - 0.0124x_2 - 0.138x_3 + 0.000014x_1x_2 + 0.00034x_1x_3 + 0.0117333x_2x_3 - 0.0000146667x_1x_2x_3$$

$$Y5 = 0.01 + 0.00015x_1 - 0.007x_2 - 0.00133333x_3 + 0.000008x_1x_2 + 0.0000466667x_1x_3 + 0.0064x_2x_3 - 0.000008x_1x_2x_3$$

$$Y6 = 0.132 - 0.00007x_1 - 0.00946667x_2 - 0.352x_3 + 0.0000113333x_1x_2 + 0.00074x_1x_3 + 0.00986667x_2x_3 - 0.0000133333x_1x_2x_3$$

Researchers note that the reponses obtained vary according to the factors study is more particularly the temperature and water vapour flow. One compares the experimental results obtained in Table 2 with the calculated results starting from the regressions equations, researchers notes a good adequacy of experimental and calculated results mentioned in Table 6. The statistics summary is mentioned in Table 7 and the results of the reponses Y1 and Y3 is represented in the Fig. 1-7.

Life Cycle Assessment (LCA): One bases oneself on the concept of durable development by providing an effective and means systemic to evaluate the environmental impacts of the activated carbon obtained according to the standard (ISO 14040, 1997).

Table 7: Table of the summarized statistics

Statistics	Y1	Y2	Y3	Y4	Y5	Y6
Manpower	8	8	8	8	8	8
Average	627.0	531.5	6.91275	0.227875	0.1225	0.17425
Standard deviation	138.006	118.189	7.04391	0.0877715	0.0337597	0.091281
Coef. of variation	22.0106%	22.2368%	101.897%	38.5174%	27.5589%	52.3851%
Minimum	425.0	359.0	1.298	0.126	0.078	0.084
Maximum	779.0	661.0	17.853	0.342	0.163	0.31
Extended	354.0	302.0	16.555	0.216	0.085	0.226
Asymmetry std.	-0.349311	-0.344387	1.1824	0.250277	-0.0637941	0.850855
Flatness std.	-1.03936	-1.05156	-0.394887	-1.14512	-1.16654	-0.656159

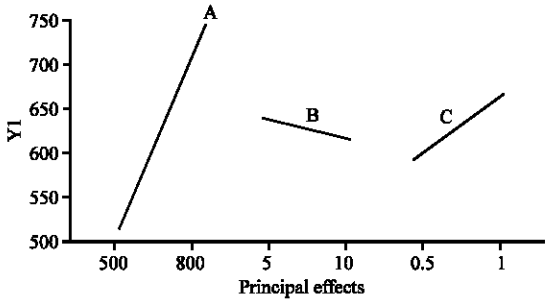

Fig. 1: Principal effects for Y1

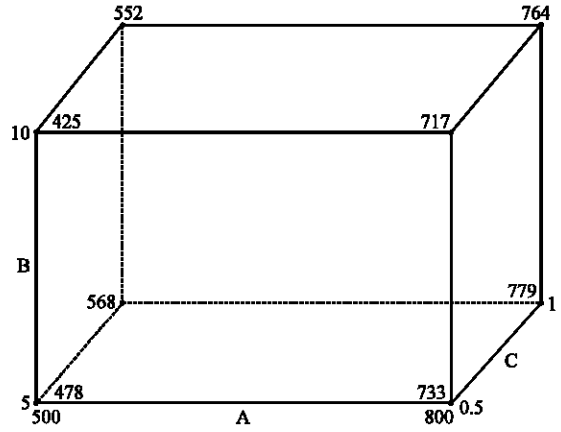

Fig. 2: Graph in cube (avarage of the data) of Y1

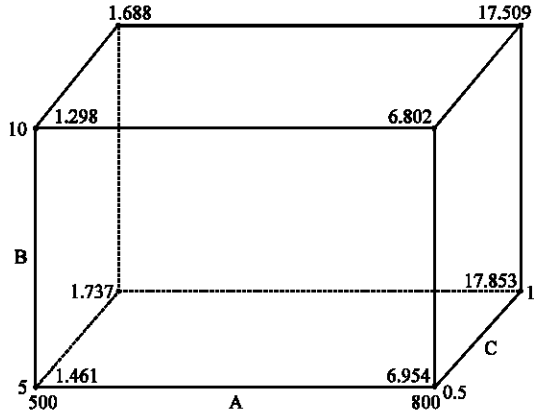

Fig. 3: Graph in cube (avarage of the data) of Y3

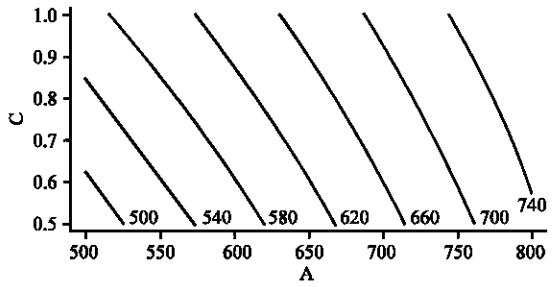

Fig. 4: Contour graph of Y1 and A-C (B = 5)

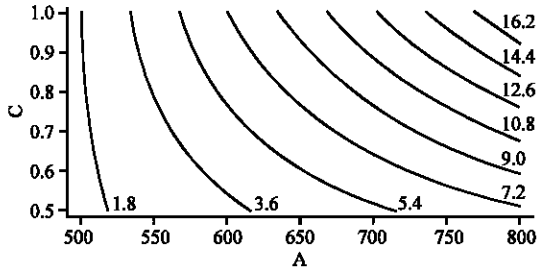

Fig. 5: Contour graph of Y3 and A-C (B = 5)

The LCA of activated carbon passes by general stages (Benoit and Mazijn, 2009), called production of olive cake residue starting from the olive-tree after olive oil extraction, sources of energy, its transport and its distribution, storage and conditioning, stages of pyrolysis of activated carbon and its use, safeguarding of the environment and finally, the good management of the life cycle of the activated carbon (recycling, destruction, storage, revalorization, etc).

Worn or saturated activated carbon can for the reactivated several times and employed again majority being. At the time of the reactivation, the pollutants are eliminated and the pores are cleaned. The activated carbon finds its activity and can be employed again.

With temperatures going until 800°C in a dedicated furnace. The carefully activated carbon is heated and reactivated by the water vapour. The pollutants are then separated. By the reactivation, researchers contribute to

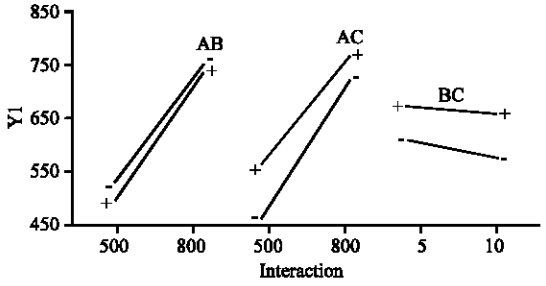

Fig. 6: Intraction diagram of Y1

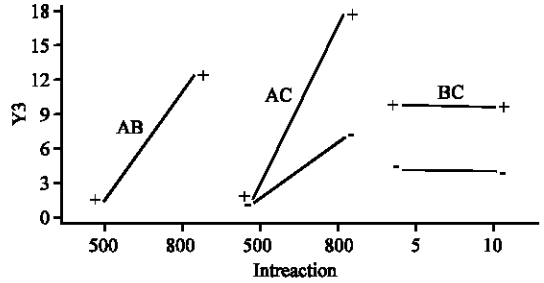

Fig. 7: Intraction diagram of Y3

Table 8: Activated carbon total production (transport, pyrolysis and activation)

System	
Indicators	Activated carbon production
Climate change (kg CO_2-eq)	3.952467331
Human health (DALY)	5.1809E-060
Ecosystem quality (PDF.m^2.y)	73.676392250
Resources (MJ)	25.315613850
Water withdrawal (m^3)	0.016167270

Table 9: Activated carbon total atmospheric emission (light, transport, pyrolysis and activation)

Indicators	Atmospheric emission
Climate change (kg CO_2-eq)	2.34
Human health (DALY)	2.884E-8
Ecosystem quality (PDF.m^2.y)	4.642E-4
Resources (MJ)	0.0479
Water withdrawal (m^3)	1.072E-5

Table 10: Assessment matter and energy (Transport = 0.777 T km^{-1})

			Leaving (kg)	
Entering	Values	Unit	Carbone	1
Olive cake residue	2.222	kg	Carbone	0.400
Electricity	0.045	kWh	CO_2	0.517
Water	0.222	L	CO	0.182
			H_2	0.012
			CH_4	0.091
			C_2H_6	0.011
			C_2H_4	0.009
			Energy	0.07 MJ

the safeguarding of the natural resources and the reduction of the emissions of CO_2 like with the durable resolution of environmental problems. With the difference of the powder activated carbon that is incinerated or put in discharge or to crush it and to mix it with the ground plants.

By assumption, the olive cake residue is regarded as organic waste. The environmental impacts analysis to produce 1 kg of activated carbon by using Quantis-suite 2.0 software (impact method 2002+vQ2.2, 2012) and the Ecoinvent basis of data is mentioned in Table 8 and 9. The matter and energy assessment to produce of 1 kg of activated carbon is mentioned in Table 10.

To interested in the impact category climatic change, researchers concludes that the production of 1 kg of activated carbon generates 3.95 kg of CO_2 as follows distributed equivalent:

- 1.59 kg during the transport stage
- 2.34 kg during the pyrolysis stage
- 0.0243 kg during the activation stage

CONCLUSION

The characterizations of the activated carbon are realized by various analyses techniques (Francis and Annick, 1998), such FTIR, DSC, ATD-ATG, CHN, BET and LANGMUIR. The obtained products are characterized by porous volumes from 0.5-0.7 cm^3 g^{-1}, average porosities from 15-20A° and specific surfaces from 400-800 m^2 g^{-1}.

The characteristics of the obtained products are comparable with the commercial activated carbon. The study of the thermal parameters and the use of factorial experimental design allowed the determination of optimum conditions for temperature, heating speed and the water vapour flow.

They result from the whole of this research that the olive cake residue is a biomass that can be useful for manufacture of the activated carbon with acceptable properties. The increasing request of the activated carbons, however relates to the field of water and the environment.

Complementary studies are in hand to highlight the use of the activated carbon in the industrial applications is more particularly in the medical sector, especially digestive purification at the time of the intoxications and researchers used in the purification of vegetable and animal oils by the elimination of the PAH (the activated carbon is obtained without uses chemicals products its activated and reactivated with proceeded the water vapour).

The study of the volatile compounds (Antonini and Hazi, 2004) formed during the preparation of the activated carbon represents the second future aspect of this research. A mathematical model of transformations making

it possible to measure the environmental impacts of the various stages of the life cycle assessment of activated carbon will be defined later.

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REFERENCES

Antonini, G. and M. Hazi, 2004. Pyrolyse-gazeification de dechets solides Partie 1. [Solid waste pyrolysis-gasification: Part 1]. Etude Ademe/ Procedis, Version V.0. June, 2004.

Benabdaah, B., J. Carre, S. Khennas, L.F. Vergnet and P. Ossoukali, 1994. Guide biomasse-energie. Edition Academia-Belgique, 1994.

Benoit, C. and B. Mazijn, 2009. Lignes Directrices Pour L'anaLyse Sociale Du Cycle De Vie Des Produits. Programmme United Nations Environment, Paris, France.

Francis, R. and R. Annick, 1998. Analyse Chimique: Methodes et Techniques Instrumentales Modernes. 4th Edn., Dunod, Paris.

Goupy, J. and L. Creighton, 2009. Introduction Aux Plans D'experiences. 4th Edn., Dunod, Paris.

Minkova, V., M. Razvigorova, E. Bjornbom, R. Zanzi, T. Budinova and N. Petrov, 2001. Effect of water vapour and biomass nature on the yield and quality of the pyrolysis products from biomass. Fuel Process. Technol., 70: 53-61.

Nefzaoui, A., 1999. Olive's tree by-products. International Center for Agricultural Research in the Dry Areas ICADRA, Edition Imprial, October, 1999.