

Energy Recovery from Solid Waste Materials via A Two-step Gasification Process by Steam

D. Vamvuka, I. Chatzifotiadis

ABSTRACT

Different biomass waste materials were gasified by steam up to 850 °C, employing a fixed bed reactor and a thermal analysis-mass spectrometer unit. Raw fuels and biochars were characterized, while bio-oil, pyrolysis gas and syngas were quantitatively analyzed. Gasification efficiency and energy potential of all solid, liquid and gaseous products were determined. The higher heating value of biochar particles, bio-oil and pyrolysis gas ranged between 16-28 MJ/kg, 21.4-33.4 MJ/kg and 10.2-13.5 MJ/m³, respectively. Organic matter was almost completely converted to syngas and lower quantities of CO₂, CH₄ and hydrocarbons upon steam gasification, with H₂ yield reaching values up to 60%. The higher heating value of syngas produced varied between 9.8 MJ/m³ and 11.4 MJ/m³.

Keywords: Biomass, energy, gasification, steam.

Published Online: March 30, 2022

ISSN: 2736-5506

DOI : 10.24018/ejenergy.2022.2.2.51

D. Vamvuka*

School of Mineral Resources Engineering,
Technical University of Crete, Chania,
Greece.

(e-mail: vamvuka@mred.tuc.gr)

H. Chatzifotiadis

School of Mineral Resources Engineering,
Technical University of Crete, Chania,
Greece.

(e-mail: liakoschat@gmail.com)

**Corresponding Author*

I. INTRODUCTION

Due to the global energy and climate crisis in recent years, increasing the share of renewable energy is urgently needed. European Green Deal is based on the deployment of renewables and decarbonized energy by 2050 [1]. Biomass, covering a wide range of materials such as agricultural, forestry, industrial and urban wastes, meets European Union policies [2], by possessing worldwide availability and versatility, low cost, carbon neutral footprint and good synergy with current coal power plants [3].

Among the thermochemical methods of converting biomass into energy, gasification with air, steam or carbon dioxide has been identified as a key technology with superior environmental performance [4]-[6] to combustion, producing a fuel gas free of unwanted side products, such as tar and char [7]-[9]. Syngas, comprising of CO and H₂, can be utilized in internal combustion engines, gas turbines, solid oxide fuel cells, or for synthesis of liquid biofuels and value-added chemicals [7], [10]-[15]. Gasification of biomass with steam, combined with a pre-pyrolysis step, not only improves the reactivity of biochar and minimizes the tar problem, but also boost the yield of H₂, leading to a higher quality gas [4], [9], [16]-[20].

The yield and composition of syngas during steam gasification depend on several factors, such as the biomass characteristics, type of gasifier and operating conditions, especially temperature and flow of steam [12], [15], [20], [21]. A smaller particle size [21], or a higher temperature [22] and steam flow [23] have been found to increase the yield and heating value of syngas. Also, inherent alkali enhanced the overall gasification reactivity [4]-[6],

[20]. Previous studies using agricultural residues [16], [17], woody and food waste [18], [19], or palm biomass [21] as raw materials reported that an increase in temperature to about 900 °C could raise the amount of H₂ in the syngas up to 47-67%, depending on steam/biomass ratio.

As most Mediterranean countries, Greece possesses a high biomass potential (3.5-5 Mtoe), which basically remains unexploited, with agricultural and forest wastes amounting about 80% [3]. Present work attempted to fulfill the requirement of recycling of these wastes for energy recovery, which is very important for national economy. Due to the limited research on combined pyrolysis and gasification processes, evaluating the energy potential of all solid, liquid and gaseous products formed, current study aimed to investigate the steam gasification of an agricultural, a forest and an industrial waste through a two-step process, employing a fixed bed reactor and a thermal analysis-mass spectrometer unit. Raw fuels and biochars were characterized, while bio-oil, pyrolysis gas and syngas were quantitatively analyzed. Gasification efficiency and the energy content of solid, liquid and gaseous species were determined.

II. MATERIALS AND METHODS

A. Selected Raw Materials

Raw materials studied were a forest residue, pine needles (NIP), collected from a forest in the region of Chania, Crete, an agro-industrial waste from a cotton ginning enterprise in Central Greece, cotton stems and seeds (COR) and an industrial waste provided from a furniture manufacturing company in West Crete, sawdust (SAW). Following air

drying, raw materials were ground in a cutting mill and sieved to a particle size below 500 μm . European standards CEN/TC335 were adopted for the characterization of the fuels, in terms of proximate analysis, ultimate analysis and calorific value.

B. Experimental Procedure of Gasification Tests

Gasification experiments were carried out in a lab-scale stainless steel fixed bed unit, with an inner diameter of 70 mm and a height of 140 mm. Prior to gasification the samples were pyrolyzed as follows. Approximately 15 g of biomass sample was loaded onto a stainless steel grid basket, supported by a rod within the reactor, which was sealed and placed into a furnace. After flushing with nitrogen for 30 min, the furnace was set to 600 $^{\circ}\text{C}$, at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ and retention time of 30 min. The sample was pyrolyzed under nitrogen of flow rate 150 mL/min, whereas its temperature was monitored by a Ni-Cr-Ni thermocouple with an accuracy ± 3 $^{\circ}\text{C}$. Volatile products were passed through salt-ice baths, to collect the condensable fractions. The reactor was cooled under nitrogen and the resulting biochar was weighed and stored.

For gasification tests, each biochar was loaded into the reactor and heated under nitrogen, as before, up to 600 $^{\circ}\text{C}$. Once reaching the desired temperature, nitrogen gas was switched to steam, by injecting distilled water with a flow rate of 0.5 mL/min, corresponding to a steam-to-biochar ratio of 3, through a syringe pump. High temperature steam was provided by a 2 m pipe surrounding the reactor, at a rate of 2500 mL/min and forced to pass through the char bed. Reaction temperature was raised to 850 $^{\circ}\text{C}$, where it was held constant for 1 h. Product gas was cooled down by passing through a cold trap, dried in a quartz filter filled up with silica gel and collected periodically for analysis during the isothermal period of 850 $^{\circ}\text{C}$, using a syringe gas tight (PTFE Luer Lock).

C. Product Analysis and Data Processing

The yield of pyrolysis products was determined by mass balance calculations. Biochars were characterized by proximate analysis, ultimate analysis and calorific value, following the same standard methods as for the raw materials. Liquid condensates were centrifuged at 6000 rpm for 20 min and bio-oil fraction was collected from the top layer and subjected to elemental analysis in a Flash 2000 CHNS analyzer. The calorific value of bio-oils (in MJ/kg) was calculated by equation [24]:

$$Q_{oil} = 0.3383C + 1.422(H - \frac{O}{8}) \quad (1)$$

In order to analyze pyrolysis gases and their energy content, raw biomass samples were pyrolyzed in a TG/DTG thermal analyzer of Perkin Elmer, connected to a quadrupole mass spectrometer (Balzers QME-200), through a heated line (200 $^{\circ}\text{C}$) encompassing a fused silicon capillary encased with a stainless steel sheath. The tests were carried out under pure argon of flow rate 35 mL/min, at a heating rate of 10 $^{\circ}\text{C}/\text{min}$, up to 600 $^{\circ}\text{C}$. The ions separated according to their mass-to-charge ratio were detected by a secondary electron multiplier (SEM) and data processing was performed by

Pyris version 3.5 and Quadstar 422 softwares. Calibration factors were determined using standard high purity gases in argon.

The yield of syngas produced from the gasification experiments was calculated by mass balance. Qualitative and quantitative analysis of product gas was performed off-line, using the mass spectrometer, as above.

III. RESULTS AND DISCUSSION

A. Characteristics of Raw Materials and Products of the Pyrolysis Step

Proximate and ultimate analysis of raw biomass materials and their biochars produced after devolatilization at 600 $^{\circ}\text{C}$ are represented in Table I. Raw fuels were rich in volatile matter, which varied between 77% and 85%. Ash content was low, particularly that of SAW, which was only 0.5%. The higher carbon and hydrogen concentrations of NIP, in conjunction with its lower oxygen concentration as compared to COR and SAW samples, resulted in a higher heating value. The sulfur and nitrogen contents of the raw materials were low to undetectable, implying insignificant emissions during thermal treatment.

After pyrolysis, Table I shows that the carbonization degree of biochars was enhanced, through the decomposition of organic matter, increasing the carbon content, while decreasing significantly the hydrogen and oxygen contents. As a result, the calorific value of NIP and COR biochars was raised by 32% to 68% with respect to raw biomass fuels. However, SAW sample lost relatively more hydrogen than oxygen during the pyrolysis process, leading to a small decrease in calorific value.

The yield of pyrolysis products of the fuels is compared in Fig. 1. NIP and COR samples generated similar amounts of biochar, but different of condensate and gas Biochar yield of SAW was lower, at the expense of that of condensate.

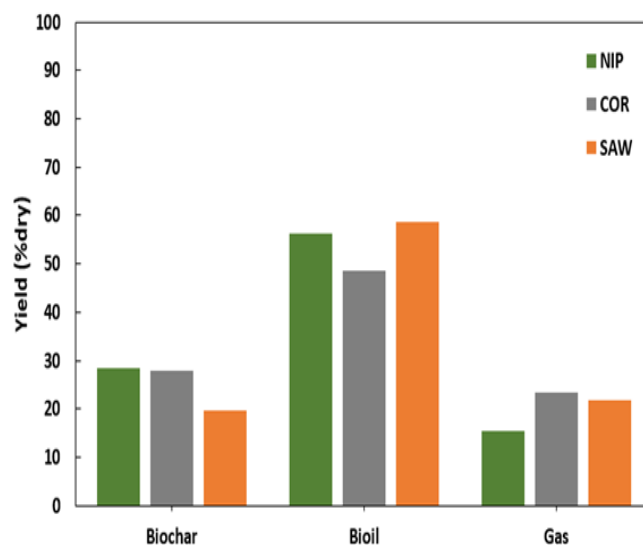


Fig1. Yield of pyrolysis products.

TABLE I: PROXIMATE AND ULTIMATE ANALYSIS OF FUELS (%DRY)

	Raw materials			Biochars		
	NIP	COR	SAW	NIP	COR	SAW
Volatiles	76.7	79.4	84.8			
Fixed carbon	17.4	15.7	14.7	79.2	82.4	97.8
Ash	5.9	4.9	0.5	20.8	17.6	2.2
C	47.7	41.6	46.2	63.2	65.6	56.3
H	6.8	6.0	6.4	1.8	1.8	2.0
N	0.2	1.1	-	1.0	0.6	-
O	39.3	46.2	46.9	13.2	14.3	39.5
S	0.07	0.24	-	-	-	-
GCV (MJ/kg)	21.1	16.4	17.4	27.7	27.5	16.1

TABLE II: PYROLYSIS PRODUCTS

	Higher heating value (MJ/kg) or (MJ/m ³)			Cumulative gas composition (m ³ /t dry biomass)				
	Biochar	Bio-oil	Gas	CO ₂	CO	CH ₄	H ₂	C _x H _y
NIP	27.7	33.4	13.5	4.0	52.0	2.0	-	1.0
COR	27.5	25.0	12.0	35.0	34.0	6.0	2.0	3.0
SAW	16.1	21.4	10.2	45.0	14.0	9.0	2.0	2.0

TABLE III: GASIFICATION PRODUCTS

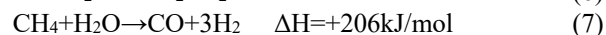
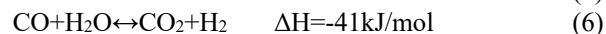
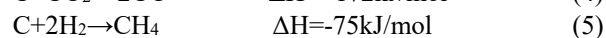
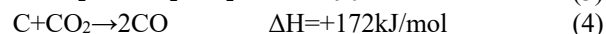
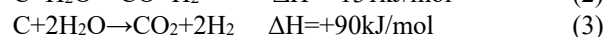
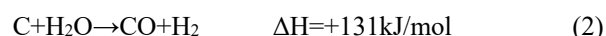
	Composition of gasification gas (%mol dry)					Higher heating value (MJ/m ³)
	H ₂	CH ₄	CO	CO ₂	C _x H _y	
NIP	22.5	0.05	66.6	10.8	0.02	11.4
COR	59.9	0.74	16.6	22.7	0.02	10.1
SAW	58.9	2.86	8.3	30.0	0.04	9.8

Table II compares the composition of pyrolysis gases as determined by the TG/MS system, as well as the heating value of gaseous, liquid and solid products of the process. Carbon dioxide was the major contributor to evolved gases and as Fig. 2 shows, the maximum evolution rate did not occur at the same temperature among the materials tested. The release of carbon dioxide occurred below 500 °C, implying breaking of C-C and C=O bonds from hemicellulose and cellulose decomposition [11]. The higher heating value of gases ranged between 10.2 MJ/m³ and 13.5 MJ/m³, with NIP presenting the highest value and SAW the lowest. The calorific value of bio-oil followed the same trend, reaching a maximum value of 33.4 MJ/kg for NIP and a minimum value of 21.4 MJ/kg for SAW.

B. Gasification Efficiency and Distribution of Product Gas

Upon gasification of the biochars with steam, Fig. 3 indicates that SAW was almost completely gasified and converted to 97% dry in syngas. For COR and NIP biochars the yield of syngas was 88% dry and 77% dry, respectively. As pyrolysis and gasification conditions were identical during the experiments for the materials studied, according to the consensus of many researchers including the authors [7], [10], [17], the principal factors that could affect the gasification reactivity of the fuels are their structural characteristics and chemical composition. A previous work by [6] showed that the surface area of SAW biochar was 5 to 8 times higher than that of COR and NIP samples. Also, the content of alkali species K and Na in COR char, known to catalyze the gasification process [9], [10], [20], was about 35 fold higher than that of NIP char, explaining its higher reactivity and conversion (100% on a dry ash free basis).

The main reactions taking place during biochar gasification under steam are summarized below:



The main gasification reaction is (2). The water gas shift reaction (6) proceeds slowly, whereas methanation reactions (5) and (7) are favored at high pressures.

The effluent concentration of the gases generated under the current experimental conditions from the three fuels studied, along with the higher heating value, are represented and compared in Table III. The product gas mixture in all cases consisted mainly of H₂ and CO, followed by CO₂ and minor quantities of CH₄ or hydrocarbons. As can be observed, COR and SAW biochars produced a similar and high amount of H₂ (59-60%), while a lower percentage of CO (8-17%) and a significant concentration of CO₂ (23-30%), as compared to the NIP biochar. Thus, for COR and SAW samples, at the high temperature of 850 °C the endothermic reactions (2) and (3) were strongly favored, increasing the formation of H₂. Moreover, the increase of H₂ concentration and concomitantly of CO₂ concentration was associated with reactions (3) and (6), due to the high steam/biochar ratio applied, revealing that excess steam promoted these reactions. The reduction of CO in this case and therefore CO decomposition was caused by the water gas shift reaction (6). The H₂ rich syngas of COR could be partly assigned to its enrichment in alkali metals K and Na [9], as previously discussed. Additionally, the H₂/CO ratio, reaching values 3.6 and 7.1 for COR and SAW, respectively, suggests that gasification of these materials could be used for chemical synthesis or biofuels production

[17], [19]. On the other hand, for NIP biochar, the syngas of which was very rich in CO, the endothermic reaction of water-gas (2), the Boudouard reaction (4) and the reverse water-gas shift reaction (6) prevailed at the high temperature, influencing the rate of formation of CO. Finally, the lower concentration of CO in SAW gas and the increased concentration in CH₄, in relation to the other fuel gases, point to the methanation reaction (7). These findings agree with reported literature data for similar fuels [12], [15], [17], [25].

As concerns the higher heating value of generated gas mixture from the steam gasification of COR, SAW and NIP biochars, Table III shows that this was higher for NIP sample (11.4 MJ/m³), which produced more combustible gas (H₂ and CO) and lower for COR and SAW samples, accordingly.

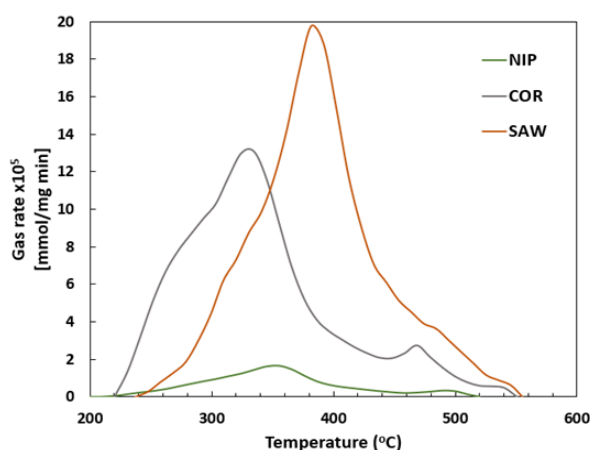


Fig. 2. Carbon dioxide evolved during pyrolysis.

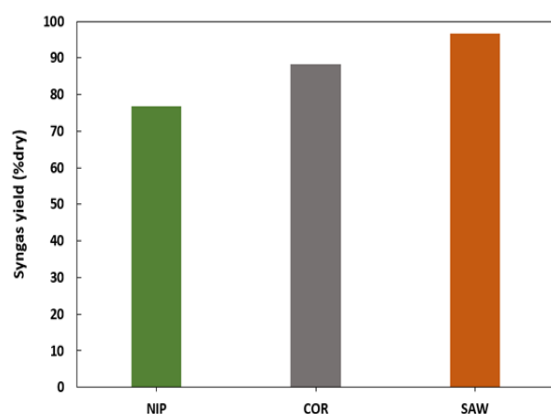


Fig. 3. Syngas production from steam gasification.

IV. CONCLUSIONS

Biomass materials studied were rich in volatile matter (77-85%) and had low ash (0.5-5.9%), nitrogen and sulfur contents. During pyrolysis up to 600 °C, CO₂, CO, H₂O_v and minor amounts of CH₄, H₂ and C_xH_y were released. The higher heating value of pyrolysis gas ranged between 10.2 MJ/m³ and 13.5 MJ/m³, whereas that of bio-oil between 21.4 MJ/kg and 33.4 MJ/kg. The carbonation degree of biochar particles was enhanced, resulting in a calorific value of ~16-28 MJ/kg. Upon steam gasification of biochars at 850 °C, organic matter was almost completely converted to

a gas mixture consisting mainly of H₂, CO, lower amounts of CO₂ and minor quantities of CH₄ and hydrocarbons. The H₂ yield of cotton residue and sawdust biochars was about 60% and the H₂/CO ratio varied between 3.6 and 7.1, suggesting a potential suitability for chemical synthesis or biofuels production. Among the samples tested, the higher heating value of gasification gas, ranging from 9.8 MJ/m³ to 11.4 MJ/m³, corresponded to pine needles fuel, which produced a more combustible gas. A further investigation using different steam/biochar ratios, for optimum performance in terms of syngas production (H₂ and CO), is required.

ACKNOWLEDGMENT

The authors kindly thank the laboratory of Hydrocarbons Chemistry and Technology of the Technical University of Crete for the ultimate analysis.

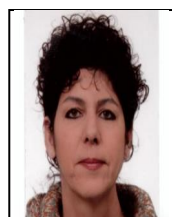
CONFLICT OF INTEREST

Authors declare that they do not have any conflict of interest.

REFERENCES

- [1] Mulvaney D. Green new deal. In: *Sol Power*. Berkley: Univ. California Press; 2019: 47-65.
- [2] Directive 2008/98/EC of the European Parliament and of the Council of 19 Nov. 2008. *Waste and repealing certain Directives*. OJL 312; 22.11.2008.
- [3] Vamvuka D. *Biomass, bioenergy and the environment*. Salonica: Tziolas Publications. 2009.
- [4] Situmorang YA, Zhao Z, Chaihai N, Wang C, Anniwaer A, Kasai Y. Steam gasification of co-pyrolysis chars from various types of biomass. *Int. J. Hydr. Energy* 2021; 46: 3640-3650.
- [5] Vamvuka d, Tefiki A, Sfakiotakis S. Increasing the reactivity of waste biochars during their co-gasification with carbon dioxide using catalysts and bio-oils. *Thermoch. Acta*. 2021; 704: 179015.
- [6] Vamvuka D, Tefiki A. Catalytic gasification of waste biomass blends with carbon dioxide. *Sci. Technol. Publ*. 2021; 5(7): 1016-1021.
- [7] Vamvuka D, Sfakiotakis S. Gasification reactivity and mass spectrometric analysis of gases of energy crop chars under CO₂ atmosphere. *Energy Fuels*. 2015; 29: 3215-3223.
- [8] Vamvuka D, Sfakiotakis S, Pantelaki O. Evaluation of gaseous and solid products from the pyrolysis of waste biomass blends for energetic and environmental applications. *Fuel*. 2019; 236: 574-582.
- [9] Cabuk B, Duman G, Yanik J, Olgun H. Effect of fuel blend composition on hydrogen yield in co-gasification of coal and non-woody biomass. *Int. J. Hydr. Energy*. 2020; 45: 3435-3443.
- [10] Ramos A, Monteiro E, Silva V, Rouboa A. Co-gasification and recent developments on waste-to-energy conversion: A review. *Renew. Sustain. Energy Rev*. 2018; 81: 380-396.
- [11] Jayaraman K, Gokalp I, Petrus S, Blandria V, Bostyn S. Energy recovery analysis from sugar cane bagasse pyrolysis and gasification using thermogravimetry, mass spectrometry and kinetic models. *J. Anal. Appl. Pyrolysis*. 2018; 132: 225-236.
- [12] Slezak R, Krzystek L, Ledakowicz S. Steam gasification of pyrolysis char from spent mushroom substrate. *Biomass Bioenergy*. 2019; 122: 336-342.
- [13] Wu H, Xiao J, Zeng X, Li X, Yang J, Zou Y, et al. A high performance direct carbon solid oxide fuel cell-a green pathway for brown coal utilization. *Appl. Energy*. 2019; 248: 679-687.
- [14] Santos RG, Alencar AC. Biomass -derived syngas production via gasification process and its catalytic conversion into fuels by Fischer Tropsch synthesis: a review. *Int. J. Hydr. Energy*. 2020; 45: 18114-18132.
- [15] Lampropoulos A, Kaklidis N, Athanasiou C, Montes-Moran MA, Arenillas A, Menendez JA, et al. Effect of olive kernel thermal treatment (torrefaction vs. slow pyrolysis) on the physicochemical

- characteristics and the CO₂ or H₂O gasification performance of as-prepared biochars. *Int. J. Hydr. Energy*. 2021; 46: 29126-29141.
- [16] Zhai M, Zhang Y, Dong P, Liu P. Characteristics of rice husk char gasification with steam. *Fuel*. 2015; 158: 42-49.
- [17] Li W, Wu S, Wu Y, Huang S, Gao J. Gasification characteristics of biomass at a high-temperature steam atmosphere. *Fuel Process. Technol.* 2019; 194: 106090.
- [18] Prasertcharoensuk P, Bull S, Phan A. Gasification of waste biomass for hydrogen production: Effects of pyrolysis parameters. *Renew. Energy*. 2019; 143: 112-120.
- [19] Nagy G, Dobo Z. Experimental investigation of fixed-bed pyrolysis and steam gasification of food waste blended with woody biomass. *Biomass Bioenergy*. 2020; 139: 105580.
- [20] Anniwaer A, Chaihad N, Zhang M, Wang C, Yu T, Kasai Y., et al. Hydrogen-rich gas production from steam co-gasification of banana peel with agricultural residues and woody biomass. *Waste Manag.* 2021; 125: 204-214.
- [21] Li Yh, Chen HH. Analysis of syngas production rate in empty fruit bunch steam gasification with varying control factors. *Int. J. Hydr. Energy*. 2018; 45: 667-675.
- [22] Islam MW. Effect of different gasifying agents (steam, H₂O₂, oxygen, CO₂ and air) on gasification parameters. *Int. J. Hydr. Energy*. 2020; 45: 31760-31774.
- [23] Parthasarathy P, Narayanan KS. Hydrogen production from steam gasification of biomass: influence of process parameters on hydrogen yield- a review. *Renew. Energy*. 2014; 66: 570-579.
- [24] Mateus MM, Gaspar D, Matos S, Reigo A, Motta C, Castenheira I, et al. Converting a residue from an edible source into a bio-oil. *J. Environ. Chem. Eng.* 2019; 7(2): 103004.
- [25] Niu Y, Han F, Chen Y, Lyu Y, Wang L. Experimental study on steam gasification of pine particles for hydrogen-rich gas. *J. Energy Inst.* 2017; 90: 715-724.



D. Vamvuka is a Chemical Engineer and Professor in the Dept. of Mineral Resources Engineering at the Technical University of Crete, where she teaches and carries out research in the field of “Solid Fuels Beneficiation and Technology”. Prof. Vamvuka’s scientific interests cover a wide spectrum of activities related to the beneficiation of solid fuels (coal, biomass, organic residues) and the new clean technologies for energy production. She has extensive experience in the fields of pyrolysis, combustion, gasification and reduction of pollutant emissions from solid fuels, as well as coal/biomass characterization and physical and chemical beneficiation.

She is the writer of about 185 scientific publications (7597 citations), several students’ publications, two books “Clean use of coals. Low rank coal technologies” (published by Ion publications) and “Biomass, Bioenergy and the Environment” (published by Tziolas publications) and two book chapters relevant to the above mentioned subjects. Until today, she has participated as a partner or coordinator in 26 National/European research and educational programs. She has been member of organizing and scientific committees for international conferences, she is member of scientific committees for energy, environment, biofuels and hydrogen, Associate Editor or member of the Editorial Board of 19 scientific journals, member of the Board of Directors of the Greek Combustion Institute, member of the Regional Council of Research and Innovation, member of the Deanery Board of the Department of Mineral Resources Engineering, Director of postgraduate studies of the Department of Mineral Resources Engineering etc. She is referee for General Secretariat of Research and Technology (GSRT) in Greece, referee of the Italian Ministry of Education, referee of 49 international scientific journals, as well as of National Research Programs.