# Slow Pyrolysis of *Cystoseira Barbata* Brown Macroalgae

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*Slow pyrolysis of algal biomass of Cystoseira barbata was performed in a fixed bed reactor using carbon dioxide as a sweeping gas and a reactant in the process. Pyrolysis products consisted of a biochar, a bio-oil, and pyrolytic gases. According to a $2^3$ factorial experiment, 8 tests were conducted for 1 hr at two levels of each process factor, i.e., specific heat flow rate (7540, 9215 W/m$^3$), carbon dioxide superficial velocity (1.3, 2.6 cm/s), and bulk density of fixed bed biomass (221, 332 kg/m$^3$). Correlations between these factors and final process responses in terms of mean bed temperature (461-663 $^o$C), biochar yield (15.2-26.7%), bio-oil yield (29.9-34.8%), and BET surface area of biochar (45.17-91.12 m$^2$/g) were established.*

*Keywords: biochar, bio-oil, Cystoseira barbata, factorial experiment, macroalgae, pyrolysis*

Macroalgae (seaweeds) are renewable and inexpensive sources of food, feed, biochemicals, biomaterials, and biofuels [1-11]. They can usually be converted into biochemicals/biomaterials by extraction and into biofuels by biochemical (alcoholic fermentation/anaerobic digestion) and thermochemical (pyrolysis/hydrothermal liquefaction) routes.

Biochar, bio-oil, and biogas can be produced by the pyrolysis of dried macroalgae. The process is usually conducted at temperatures up to 1000 $^o$C and atmospheric pressure, in the presence of a carrier gas [1,9,12-19]. Distribution, composition, properties, and applications of the pyrolysis products mainly depend on algal species, its composition and pre-treatment, as well as on reaction conditions (*e.g.*, heating rate, temperature, type and flow rate of carrier gas). Slow pyrolysis (heating rates of up to 40 °C/min) of macroalgal biomass generally leads to a biochar production of 19-68% and a bio-oil yield of up to 47% [1,9,12,13,15,17,19].

The bio-oil has a high content of oxygenates (*e.g.*, phenols, ketones, aldehydes, alcohols, carboxylic acids, furans) and a low amount of hydrocarbons, resulting in a relatively low heating value (HHV of 20-30 MJ/kg) [1,9]. It can be combusted or upgraded to obtain combustibles and chemicals.

The biochar is suitable as a renewable fuel, adsorbent, soil amender, precursor for making catalyst or activated carbon [13,15,20-23]. Biochar characterization as well as experimental study and prediction of the effect of pyrolysis conditions on biochar yield and properties are essential for optimizing and tailoring its properties for using in appropriate applications.

This paper has aimed at studying the fixed bed pyrolysis of dried and crushed algal biomass of *Cystoseira barbata*, a brown macroalga growing along the Romanian coast of Black Sea [24-26], under carbon dioxide atmosphere. The effects of process independent variables, *i.e.*, specific heat flow rate, carbon dioxide superficial velocity, and bulk bed density, on the process dynamics and final values of bed temperature, yields of pyrolysis products, and BET surface area of biochar were evaluated.

## Experimental part

### *Materials*

Samples of *Cystoseira barbata* were harvested on the Romanian Black Sea shore, washed with distilled water, dried to a constant weight at 45$^o$C, and further crushed and sieved to mean particle sizes of 0.8 mm and 1.5 mm.

### *Equipment and procedure*

Laboratory set-up employed for experimental study of slow pyrolysis was presented in our previous papers [27,28]. Dried and crushed algal biomass was packed in a quartz column (5 cm internal diameter and 50 cm height). Column external wall, which was thermally insulated, was heated by an electric resistance, resulting in the heating and decomposition of vegetal material. Carbon dioxide up-flowed through the fixed bed algal biomass and left the column along with the volatiles (vapour and permanent gases) obtained during the pyrolysis. The volatiles were cooled in a condenser, resulting in bio-oil and non-condensable gases. The biochar obtained in the pyrolysis process was analyzed using an ASAP 2020 Micromeritics Surface Area and Porosity Analyzer.

### *Experimental variables*

Vegetal material mass, $m$, bio-oil mass, $m_{oil}$, bed centre temperature, $t_c$, and column wall temperature, $t_w$, were continuously recorded as a function of heating time, $\tau$. Experimental studies were conducted for 1 hr at two levels of each process factor, *i.e.*, specific heat flow rate ($P$=7540, 9215 W/m$^3$), expressed as heat flow rate divided by the volume of fixed bed biomass, carbon dioxide superficial velocity ($w$=1.3, 2.6 cm/s), and bulk bed density ($\rho$=221, 332 kg/m$^3$). Low and high levels of $\rho$ correspond to coarser (1.5 mm) and finer (0.8 mm) biomass particles, respectively. 8 tests of slow pyrolysis were carried out according to a $2^3$ factorial plan (table 1). BET surface area of biochar obtained in each experiment was also determined.

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## Results and discussions

*Pyrolysis experimental curves*

Dynamics of specific mass of algal biomass, $m/m_0$, and bio-oil, $m_{oil}/m_0$, where $m_0$ represents the initial macroalga mass, as well as those of logarithmic mean bed temperature defined by eq. (1), $t_m$, shown in figures 1-3, highlight the following aspects: (i) the solid mass generally increased with an increase in bulk density ($\rho$) and a decrease in specific heat flow rate ($P$), irrespective of time ($\tau$); (ii) the production of biochar (at $\tau$=60 min), $m_f/m_0$, was larger at a high level of gas superficial velocity ($w$); (iii) the bio-oil mass and mean bed temperature generally increased with $P$, irrespective of time. Moreover, the final values of specific mass of algal biomass ($m_f/m_0$=0.152-0.267) and bio-oil ($m_{oil}/m_0$=0.299-0.348) were quite similar with those reported in our previous study on the slow pyrolysis of lignocellulosic biomass, *i.e.*, sorghum stalk and leaves [29].

$$t_m = \frac{t_w - t_c}{\ln \frac{t_w}{t_c}} \qquad (1)$$

Variation rate of volatile matter conversion, $d\alpha/d\tau$, where $\alpha$ is defined by eq. (2), depending on mean bed temperature, $t_m$, is depicted in figure 4. According to the data reported in the related literature, each differential curve in figure 4 has three peaks [12,14,16-19]. Maximal values of $d\alpha/d\tau$, $(d\alpha/d\tau)_{peak}$, and those of corresponding mean bed temperature, $t_{m,peak}$, under various operation conditions are summarized in table 1. The first peak (with a maximum of 0.022-0.054 min$^{-1}$ at $t_{m,peak1}$=119-164°C) is an effect of biomass moisture removal. The second peak (with a maximum of 0.037-0.061 min$^{-1}$ at $t_{m,peak2}$=288-350°C) is due to carbohydrates decomposition, whereas the third peak (with a maximum of 0.007-0.039 min$^{-1}$ at $t_{m,peak3}$=430-488°C) is due to proteins decomposition [12,18]. It is observed that the second peak is higher than the third, indicating a higher amount of carbohydrates. Analysis of samples of *Cystoseira barbata* harvested on the Romanian Black Sea shore revealed 58.1% carbohydrates, 14.1% proteins, 1% fats, and 17.6% ash [30].

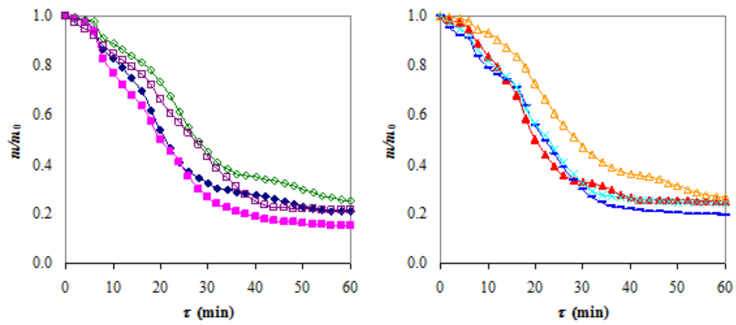


Fig. 1. Dynamics of specific mass of algal biomass: ♦exp 1, ■ exp 2, ▲ exp 3, - exp 4, ◊exp 5, □exp 6, △ exp 7, × exp 8)

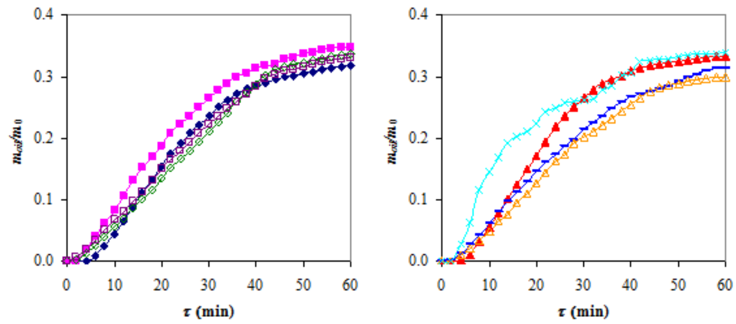


Fig. 2. Dynamics of specific mass of bio-oil: ♦exp 1, ■ exp 2, ▲ exp 3, - exp 4, ◊exp 5, □exp 6, △ exp 7, × exp 8)

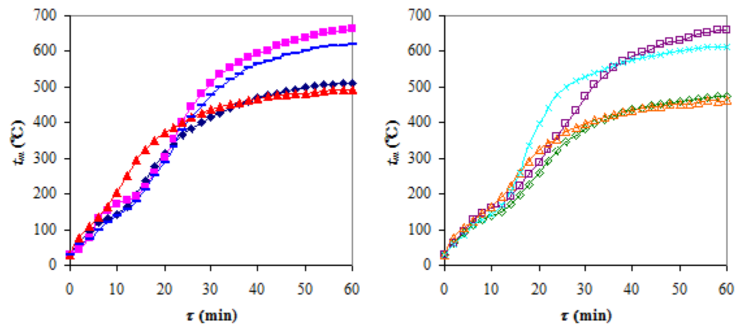


Fig. 3. Dynamics of mean bed temperature: ♦exp 1, ■ exp 2, ▲ exp 3, - exp 4, ◊exp 5, □exp 6, △ exp 7, × exp 8)

**Table 1**
MAXIMAL VALUES OF VARIATION RATE OF VOLATILE MATTER CONVERSION AND CORRESPONDING MEAN BED TEMPERATURE FOR THREE MAIN STAGES OF DECOMPOSITION OF ALGAL BIOMASS

| Exp. | $P$ (W/m$^3$) | $w$ (cm/s) | $\rho$ (kg/m$^3$) | $(d\alpha/d\tau)_{peak1}$ (min$^{-1}$) | $t_{m,peak1}$ (°C) | $(d\alpha/d\tau)_{peak2}$ (min$^{-1}$) | $t_{m,peak2}$ (°C) | $(d\alpha/d\tau)_{peak3}$ (min$^{-1}$) | $t_{m,peak3}$ (°C) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 7540 | 1.3 | 221 | 0.048 | 130 | 0.051 | 312 | 0.007 | 488 |
| 2 | 9215 | 1.3 | 221 | 0.054 | 154 | 0.042 | 304 | 0.034 | 444 |
| 3 | 7540 | 2.6 | 221 | 0.041 | 164 | 0.061 | 350 | 0.015 | 462 |
| 4 | 9215 | 2.6 | 221 | 0.047 | 119 | 0.048 | 288 | 0.035 | 430 |
| 5 | 7540 | 1.3 | 322 | 0.045 | 127 | 0.042 | 330 | 0.009 | 463 |
| 6 | 9215 | 1.3 | 322 | 0.027 | 147 | 0.037 | 324 | 0.032 | 473 |
| 7 | 7540 | 2.6 | 322 | 0.022 | 145 | 0.040 | 344 | 0.008 | 456 |
| 8 | 9215 | 2.6 | 322 | 0.036 | 129 | 0.054 | 335 | 0.039 | 478 |

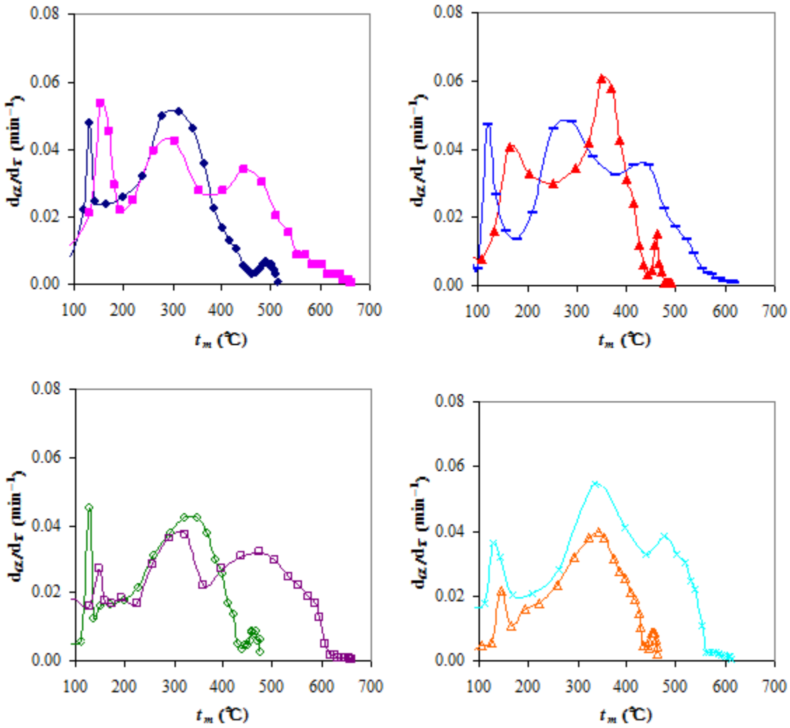


Fig. 4. Variation rate of volatile matter conversion *vs.* mean bed temperature: ♦exp 1, ■ exp 2, ▲ exp 3, - exp 4, ◊exp 5, □exp 6, △ exp 7, × exp 8)

**Table 2**
EXPERIMENTATION MATRIX

| Exp. | $P$ (W/m³) | $w$ (cm/s) | $\rho$ (kg/m³) | $x_1$ | $x_2$ | $x_3$ | $m_f/m_0$ (g/g) | $m_{oilf}/m_0$ (g/g) | $t_{mf}$ (°C) | $S_{BET}$ (m²/g) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 7540 | 1.3 | 221 | -1 | -1 | -1 | 0.208 | 0.317 | 512 | 91.12 |
| 2 | 9215 | 1.3 | 221 | 1 | -1 | -1 | 0.152 | 0.348 | 663 | 55.49 |
| 3 | 7540 | 2.6 | 221 | -1 | 1 | -1 | 0.250 | 0.332 | 491 | 88.81 |
| 4 | 9215 | 2.6 | 221 | 1 | 1 | -1 | 0.196 | 0.313 | 619 | 50.04 |
| 5 | 7540 | 1.3 | 322 | -1 | -1 | 1 | 0.251 | 0.337 | 473 | 86.23 |
| 6 | 9215 | 1.3 | 322 | 1 | -1 | 1 | 0.213 | 0.330 | 661 | 51.41 |
| 7 | 7540 | 2.6 | 322 | -1 | 1 | 1 | 0.267 | 0.299 | 461 | 80.51 |
| 8 | 9215 | 2.6 | 322 | 1 | 1 | 1 | 0.243 | 0.338 | 612 | 45.17 |

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \qquad (2)$$

*Biochar characterization*

The values of BET surface area of biochar obtained in the pyrolysis process, $S_{BET}$ (m²/g), depending on the process factors, $P$, $w$, and ρ, are specified in table 2. Tabulated results highlight lower $S_{BET}$ values for higher levels of all process factors. Moreover, the values of BET surface area ($S_{BET}$=45.17-91.12 m²/g) are consistent with those reported in the related literature [13,15].

*Prediction of process performances*

A statistical model based on a $2^3$ factorial plan was used to establish the dependences between the dimensionless process factors expressed by eqs. (3)-(5) and final ($f$) values of process responses in terms of biochar yield, $m_f/m_0$, bio-oil yield, $m_{oilf}/m_0$, mean bed temperature, $t_{mf}$, and BET surface area of biochar, $S_{BET}$. Values of process factors and final responses are summarized in table 2. Tabulated data were processing according to characteristic procedure of a $2^3$ factorial experiment resulting in eqs. (6)-(9). The significance of regression coefficients in eqs. (6)-(9) was tested using the Student test [31-34]. Eqs. (10)-(13), which were obtained by eliminating the non-significant coefficients, reveal that: (i) biochar yield ($m_f/m_0$) increases with an increase in gas superficial velocity ($x_2$) and fixed bed density ($x_3$) as well as with a decrease in specific heat flow rate ($x_1$); (ii) final bio-oil yield ($m_{oilf}/m_0$) increases with an increase in $x_1$ and $x_1x_2x_3$ interaction as well as with a decrease in $x_2$; (iii) final value of mean bed temperature ($t_{mf}$) increases with an increase in $x_1$ as well as with a decrease in $x_2$ and $x_3$, the effect of $x_1$ being significant; (iv) BET surface areas of biochar ($S_{BET}$) are larger for lower values of all process factors and the effect of $x_1$ is significant.

$$x_1 = \frac{P - 8377}{837.5} \qquad (3)$$

$$x_2 = \frac{w - 1.95}{0.65} \qquad (4)$$

$$x_3 = \frac{\rho - 276.5}{55.5} \qquad (5)$$

$$m_f / m_0 = 0.222 - 0.022x_1 + 0.017x_2 + 0.021x_3 + 0.002x_1x_2 + 0.006x_1x_3 - 0.005x_2x_3 + 0.002x_1x_2x_3 \qquad (6)$$

$$m_{oilf} / m_0 = 0.327 + 0.006x_1 - 0.006x_2 - 0.001x_3 - 0.001x_1x_2 + 0.003x_1x_3 - 0.001x_2x_3 + 0.012x_1x_2x_3 \qquad (7)$$

$$t_{mf} = 561.5 + 77.25x_1 - 15.75x_2 - 9.75x_3 - 7.50x_1x_2 + 7.50x_1x_3 + 0.50x_2x_3 - 1.75x_1x_2x_3 \quad (8)$$

$$S_{BET} = 68.60 - 18.07x_1 - 2.465x_2 - 2.768x_3 - 0.457x_1x_2 + 0.530x_1x_3 - 0.525x_2x_3 + 0.328x_1x_2x_3 \quad (9)$$

$$m_f / m_0 = 0.222 - 0.022x_1 + 0.017x_2 + 0.021x_3 \quad (10)$$

$$m_{oilf} / m_0 = 0.327 + 0.006x_1 - 0.006x_2 + 0.012x_1x_2x_3 \quad (11)$$

$$t_{mf} = 561.5 + 77.25x_1 - 15.75x_2 - 9.75x_3 \quad (12)$$

$$S_{BET} = 68.60 - 18.07x_1 - 2.465x_2 - 2.768x_3 \quad (13)$$

## Conclusions

Slow pyrolysis of algal biomass of *Cystoseira barbata* was conducted for 1 hr under various conditions resulting in biochar (15.2-16.7%), bio-oil (29.9-34.8%), and pyrolytic gases. Carbon dioxide was employed as a sweeping gas and a reactant in the fixed bed pyrolysis.

Specific heat flow rate ($P$=7540, 9215 W/m$^3$), carbon dioxide superficial velocity ($w$=1.3, 2.6 cm/s), and bulk density of fixed bed biomass ($\rho$ =221, 332 kg/m$^3$) were selected as process factors. A statistical model based on a $2^3$ factorial plan was used to establish correlations between the process factors and its final responses in terms of mean bed temperature ($t_{mf}$=461-663°C), biochar yield ($m_f/m_0$=0.152-0.267), bio-oil yield ($m_{oilf}/m_0$=0.299-0.348), and BET surface area of biochar ($S_{BET}$=45.17-91.12 m$^2$/g). Final bed temperature increased significantly with specific heat flow rate resulting in an increase in bio-oil production and a decrease in that of biochar. An increase in gas superficial velocity determined lower bed temperature and bio-oil yield as well as a higher biochar yield. An increase in bulk density led to a lower bed temperature and a larger biochar amount. BET surface areas of biochar were higher for lower values of all process factors. This statistical model could be used to predict the process performance for values of process factors in the ranges considered in the experimental study.

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## References

1. CHEN, H., ZHOU, D., LUO, G., ZHANG, S., CHEN, J., Renew. Sust. Energ. Rev., **47**, 2015, p. 427.
2. CHO, Y.K., KIM, M.J., KIM, S.K., Korean Soc. Biotechnol. Bioeng. J., **28**, no. 6, 2013, p. 366.
3. HOLDT, S.L., KRAAN, S., J. Appl. Phycol., **23**, 2011, p. 543.
4. JIANG, R., INGLE, K.N., GOLBERG, A., Algal Res., **14**, 2016, p. 48.
5. JUNG, K.A., LIM, S.R., KIM, Y., PARK, J.M., Bioresour. Technol., **135**, 2013, p. 182.
6. NEIFAR, M., CHATTER, R., CHOUCHANE, H., GENOUIZ, R., JAOUANI, A., MASMOUDI, A.S., CHERIF, A., AIMS Bioengineering, **3**, no. 3, 2016, p. 400.
7. SILVA, M. VIEIRA, L., ALMEIDA, A.P., KIJJOA, A., Oceanography, **1**, no. 1, 2013, p. 1.
8. SIRAJUNNISA, A.R., SURENDHIRAN, D., Renew. Sust. Energ. Rev., **66**, 2016, p. 248.
9. SONG, M., PHAM, H.D., SEON J., WOO, H.C., Renew. Sust. Energ. Rew., **50**, 2015, p. 782.
10. TRIVEDI, N., GUPTA, V., REDDY, C.R.K., JHA, B., Marine Macroalgal Biomass as a Renewable Source of Bioethanol (Chapter 11) in Marine Bioenergy Trends and Developments (Eds. S.K. Kim and C.G. Lee), CRC Press, 2015, p. 197.
11. VASSILEV, S.V., VASSILEVA, C.G., Fuel, **181**, 2016, p.1.
12. BAE, Y.J., RYU, C., JEON, J.K., PARK, J., SUH, D.J., SUH, Y.W., CHANG, D., PARK, Y.K., Bioresour. Technol., **102**, 2011, p. 3512.
13. BIRD, M.I., WURSTER, C.M., de PAULA SILVA, P.H., BASS, A.M., de NYS, R., Bioresour. Technol., **102**, 2011, p. 1886.
14. CEYLAN, S., GOLDFARB, J.L., Energ. Convers. Manage., **101**, 2015, p. 263.
15. JUNG, K.W., KIM, K., JEONG, T.U., AHN, K.H., Bioresour. Technol., **200**, 2016, p. 1024.
16. KIM, S.S., LY, H.V., CHOI, G.H., KIM, J., WOO, H.C., Bioresour. Technol., **123**, 2012, p. 445.
17. KIM, S.S., LY, H.V., KIM, J., CHOI, J.H., WOO, H.C., Bioresour. Technol., **139**, 2013, p. 242.
18. ROSS, A.B., JONES, J.M., KUBACKI, M.L., BRIDGEMAN, T., Bioresour. Technol., **99**, 2008, p. 6494.
19. ZHU, Y., KWONG, C.W., van EYK, P.J., de NYS, R., WANG, D., ASHMAN, P.J., Energy Fuels, **29**, 2015, p. 5047.
20. CEATRA, L., PARVULESCU, O.C., RODRIGUEZ RAMOS, I., DOBRE, T., Ind. Eng. Chem. Res., **55**, no. 6, 2016, p. 1491.
21. JANUS, A., PELFRENE, A., HEYMANS, S., DEBOFFE, C., DOUAY, F., WATERLOT, C., J. Environ. Manage., **162**, 2015, p. 275.
22. KUPPUSAMY, S., THAVAMANI, P., MEGHARAJ, M., VENKATESWARLU, K., NAIDU, R., Environ. Int., **87**, 2016, p. 1.
23. QIAN, K., KUMAR, A., ZHANG, H., BELLMER, D., HUHNKE, R., Renew. Sustainable Energy Rev., **42**, 2015, p. 1055.
24. MARIN, O., ABAZA, V., SAVA, D., Marine Research, **43**, 2013, p. 197.
25. MARIN, O., SAVA, D., SAMARGIU, M., Scientific Studies and Research, Series Biology, **24**, no.1, 2015, p. 27.
26. MARIN, O., TIMOFTE, F., Atlas of Macrophytes on the Romanian Sea Shore, Boldas, Constanta, 2011.
27. DOBRE, T., PÂRVULESCU, O.C., IAVORSCHI, G., STOICA, A., STROESCU, M., International Journal of Chemical Reactor Engineering, **8**, 2010, p. 1968.
28. PARVULESCU, O.C., DOBRE, T., CEATRA, L., IAVORSCHI, G., MIREA, R., Rev. Chim. (Bucharest), **62**, no. 1, 2011, p. 89.
29. PARVULESCU, O.C., GAVRILA, A.I., DOBRE, T., CEATRA, L., Rev. Chim. (Bucharest), **67**, no. 11, 2016, p. 2254.
30. *** INCDM Grigore Antipa, Project MACROEVAL, Research report no. 3. Structural characterization of macrophytes on the Romanian sea shore, 2010, http://www.rmri.ro/WebPages/MACROEVAL/32-144%20Etapa3.pdf.
31. ARUS, A.V., NISTOR, I.D., PLATON, N., ROSU, A.M., MUNTIANU, G., JINESCU, C., Rev. Chim. (Bucharest), **66**, no. 1, 2015, p. 88.
32. CIOROIU, D.R., PARVULESCU, O.C., KONGSAG, C.I., DOBRE, T., Rev. Chim. (Bucharest), **68**, no. 10, 2017, p. 2311.
33. ION, V.A., PARVULESCU, O.C., DOBRE, T., Appl. Surf. Sci., **335**, 2015, p. 137.
34. ORBECI, C., PARVULESCU, O.C., ACCELEANU, E., DOBRE, T., Rev. Chim. (Bucharest), **68**, no. 10, 2017, p. 2325.

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