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Energetic Willow (*Salix viminalis*) – Unconventional Applications

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1. Introduction

Salix viminalis (Common Osier, Basket Willow, Energetic Willow) is a plant belonging to the SRWC group (Short Rotation Woody Crops) (Borjesson et al., 1994; Christersson & Sennerby-Forsse, 1994). Such a qualification points out possible applications resulting from a fast growth and annual yield of biomass. The woody stems of *Salix viminalis* can be cut frequently and serve as burnable biomass. Therefore *Salix viminalis* wood is often called a “green fuel”. In general, willows (genus *Salix*) are popular plants since more than 400 species occur in Nature (including *Salix viminalis*). Particularly, Northern Hemisphere is a natural region for different willow species bearing sometimes traditional and very unique names like Sageleaf Willow, Goat Willow, Pussy Willow, Coastal Plain Willow, Kimura, Grey Willow, Sand Dune Willow, Furry Willow, Heartleaf Willow, Del Norte Willow, American Willow, Drummond's Willow, Eastwood's Willow, Mountain Willow, Sierra Willow etc. The variety of willow species partly results from ease of hybrid formation by cross-fertile of particular *Salix* genotypes in a natural process and/or by planned cultivation. Table 1 contains systematic botanic classification of willows.

| | |
|---------|--------------|
| Kingdom | Plantae |
| Order | Malpighiales |
| Family | Salicaceae |
| Tribe | Salicaceae |
| Genus | Salix |

Table 1. Botanic classification.

The differences between *Salix* species also consists in the morphology of willows i. e. scrubs and trees naturally occur. In practice moist soils and mild climate conditions suits perfectly the demands of willows.

2. *Salix viminalis* – Conventional applications

2.1 Energetic utilization

In the recent decades among all *Salix* genotypes particularly *Salix viminalis* gained most attention as a agriculturally cultivated plant due to its application as a green fuel. Several positive and negative aspects of such an application are summarized in table 2.

| Positive arguments | Negative arguments |
|---|---|
| High fertility and yield High environmental tolerance Long exploitation of plantations Low labor consumption and advantageous year schedule on labor demand during cultivation Improvement of local economy Reduction of unemployment Diversification of energy resources Low capital consumption during vegetation High energetic effectiveness Reduced consumption of conventional fuels Environment friendly biomass utilization for energetic purposes Exploitation of lie fallows Efficient assimilation of heavy metals Possible cultivation on soils unusable for other crops Possible reclamation of deteriorated lands Constant price increase of fossil fuels Increase of ecological awareness of the society Financial support from EU and local institutions | High cost of plantation lodging Lost of financial fluency due to high cost of the preliminary stage of undertaking Difficult prediction of investment return Lack of integrated bio-energy consumer market High transportation cost from plantation Necessity of fast utilization after harvesting Better cost efficiency of coal originated energy Energy overproduction High cost of biomass agglomerate fabrication High volume of biomass High nitrogen content in fresh harvested biomass High moisture content in fresh harvested biomass Threats resulting form monoculture cultivation on large agriculture areas Unexpected weather and climate changes Damages caused by diseases and pests |

Table 2. Selected positive and negative aspects of energetic willow (*Salix viminalis*) cultivation. Particular points in the table selected from the original content. Cited and translated after (Zabrocki & Ignacek, 2008).

Many of the above mentioned arguments result in fact from economic, social and political background. Thus, the cultivation of *Salix viminalis* may definitely find numerous supporters but also opponents. However, positive features of *Salix viminalis* cultivation must be kept in mind since they may help to solve some critical environmental and social issues. In some countries the cultivation and usage of Energetic Willow is at very limited level (Poland). Some sources claim (Bio-energia, 2008) that overall *Salix viminalis* cultivation area does not exceed 6000 hectares. The share of *Salix viminalis* wood burned as a fuel in the total mass of burnable fuels is only ca. 2% high. The situation has not changed significantly in the last period despite of competitive energetic (table 3) and economic (table 4) parameters of the fuel.

| Fuel | Heat of combustion [GJ/1000 kg] |
|-----------------------------------|---------------------------------|
| LPG | ca. 45 |
| Fuel oil (light fraction) | ca. 42 |
| Fuel oil (heavy fraction) | ca. 40 |
| Black coal | ca. 27 |
| Coke | ca. 25 |
| Dry wood (incl. Energetic Willow) | ca. 19 |
| Dry straw | ca. 15 |

Table 3. Heat of combustion of selected fuels. The content of the table selected from the original material and translated (Iso-Tech, 2011).

| Plant | Plantation no. | Harvest frequency* | Dry biomass price | |
|------------------|----------------|--------------------|-------------------------|--------------------------|
| | | | Netto [PLN** / 1000 kg] | Brutto [PLN** / 1000 kg] |
| Energetic Willow | 8 | 1 | 367 | 491 |
| | | 2 | 333 | 458 |
| | | 3 | 253 | 356 |
| Energetic Willow | 9 | 1 | 346 | 447 |
| | | 2 | 335 | 444 |
| | | 3 | 247 | 337 |

*Harvest frequency: 1 - each year, 2 - every 2 years, 3 - every 3 years

**PLN - currency of Poland, 1 EUR = 4 PLN

Source: <http://www.bio-energia.pl/>

Table 4. Dry biomass prices in Poland. The content of the table selected from the original source and translated (Bio-energia, 2008).

Thus, 1000 kg of dry *Salix viminalis* wood offers amount of energy comparable to 700 kg of black coal of good quality. However, black coal mining is evidently associated with serious irreversible environmental damages what becomes more and more important issue nowadays. This is a next argument for increasing of biomass production and usage for energetic purposes. Energetic utilization of other plants from SRWC group like *Plantanus occidentalis*, *Liquidambar styraciflua*, *Pennisetum purpureum*, *Erianthus arundenaceum*, *Panicum virgatum*, *Ricinus communis*, *Hibiscus cannabinnis*, *Populus deltoids*, *Pinus elliottii*, *Eucalyptus amplifolis*, *Eucalyptus grandis*, or *Pinus taeda* is a much more rare case in the world scale and particularly in Europe where climate conditions are often the main limiting factor. In Europe, *Salix viminalis* wood seen as renewable source of “green fuel” has a one important competitor i. e. dry straw. Straw is a side product (ca. 20 billion kg per annum in Poland) of grains cultivation i. e. one of the most frequent agricultural activities (Gradziuk, 1999).

2.2 Environment protection - Phytoremediation

Phytoremediation of soil and waters is a task of numerous research projects and technological undertakings. Such attempts base on an unique feature of *Salix viminalis* i. e. the ability to effective uptake, deactivation and accumulation of relatively high amounts of

heavy metals without losing its vitality. The efficiency of metal ion accumulation is extraordinarily high if compared to other plants and microorganisms. Therefore *Salix viminalis* is often called "hyper-accumulator". This point let to state that *Salix viminalis* is a unique plant among other energetic plants which mainly offer only a high growth rate and mass production but are poor metal ion accumulators.

Memon et al., 2001 citing other authors stated that retention of heavy metals may be accounted to one the below mentioned technologies (Salt et al., 1995; Pilon-Smits & Pilon, 2000):

1. Phytoextraction, in which metal-accumulating plants are used to transport and concentrate metals from soil into the harvestable parts of roots and above-ground shoots (Brown et al., 1994; Kumar et al., 1995).
2. Rhizofiltration, in which plant roots absorb, precipitate and concentrate toxic metals from polluted effluents (Smith & Bradshaw, 1979); Dushenkov et al., 1995).
3. Phytostabilization, in which heavy metal tolerant plants are used to reduce the mobility of heavy metals, thereby reducing the risk of further environmental degradation by leaching into the ground water or by airborne spread (Smith & Bradshaw, 1979; Kumar et al., 1995).
4. Plant assisted bioremediation, in which plant roots in conjunction with their rhizospheric microorganisms are used to remediate soils contaminated with organics (Walton & Anderson, 1992; Anderson et al., 1993).

In the case of *Salix viminalis* the process of metal ion accumulation proceeds through a root system and ion transport involving vascular tissues in stems and differentiated distribution in the whole plant body. Permeation of ions into roots is a typical way of efficient metal ion collection by *Salix viminalis*. This a basis for practical utilization of *Salix viminalis* for purification of various matrixes (soil, water, etc.) being in contact with roots of the plant. Planting of *Salix viminalis* on metal contaminated soils and/or bringing the plant in contact with contaminated waters lead to slow but constant removal of the metal impurities and finally remediation of soil and waters.

According to Baker & Walker, 1990 plants may follow three pathways when they grow on metal contaminated soils.

1. Metal excluders: aerial parts of these plants are free from metal contamination despite of high concentration of them in the soil and in the roots.
2. Metal indicators: such plants accumulate metals in their aerial parts and the concentration of metals depends on the metal content in the soil.
3. Accumulators and hyperaccumulators: These plants concentrate metals in their aerial part but the metal content in the tissues exceeds metal content in the soil. A plant capable to accumulate more than 0.1% of Ni, Co, Cu, Cr or Pb or 1% of Zn (despite of differences in metal content in the soil) in its leaves (dry mass) is called a hyperaccumulator. *Salix viminalis*, according to our earlier studies, may be accounted to the accumulators / hyperaccumulators category. Figs 1 and 2 present (Łukaszewicz et al., 2009) some of our results on the concentration of selected metal ions (Zn^{2+} , Cu^{2+} , Cr^{3+}) in different parts of *Salix viminalis* rods after a certain time of contact with water solutions of the ions.

Table 5 shows that example heavy metal ions (Cu^{2+}) penetrate all important parts of *Salix viminalis*. The ion penetration and the resulting copper accumulation increase with increasing concentration of Cu^{2+} in an artificial soil. Plants were incubated in complete

Knop's medium (Reski & Abel, 1985) containing copper salt at 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 mM stabilized with quartz sand in hydroponic pots. It is also visible that roots and rods (stems) i. e. plant parts responsible for metal ion transportation accumulate copper ions more intensively than new shoots and leaves. The latter parts are rather a final location of metal ions and do not participate significantly in the ion transportation. Table 5 informs about biometric changes of the plants exposed to Cu^{2+} infiltration. The plants were still living but shoots, leaves and roots underwent a gradual degradation consisting in reduction of mass and/or dimensions. Table 6 (Mleczek et al., 2009) considers the dependence between the kind of metal ion and its accumulation in different tissues. No strict correlation is visible except general tendency to intensive accumulation of cadmium and chromium.

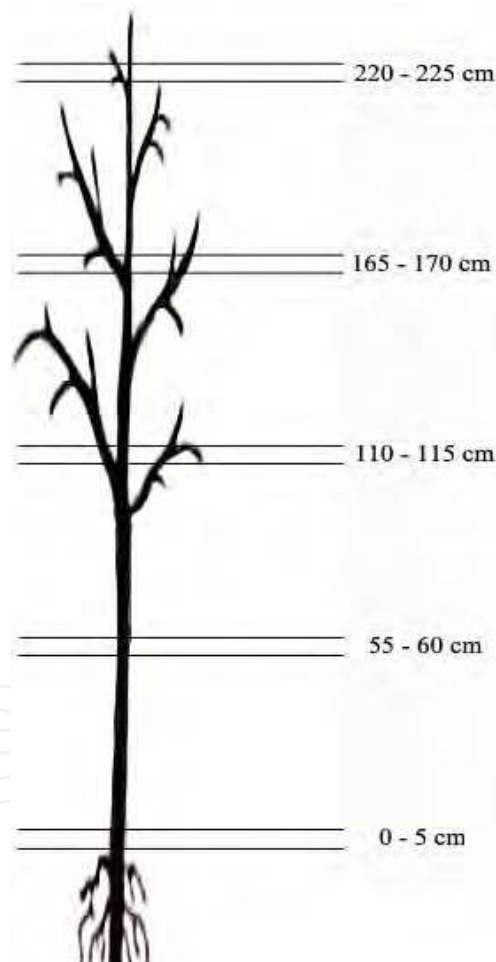


Fig. 1. Sampling wood material from *Salix viminalis* species planted in metal ions solutions. (Łukaszewicz et al., 2009).

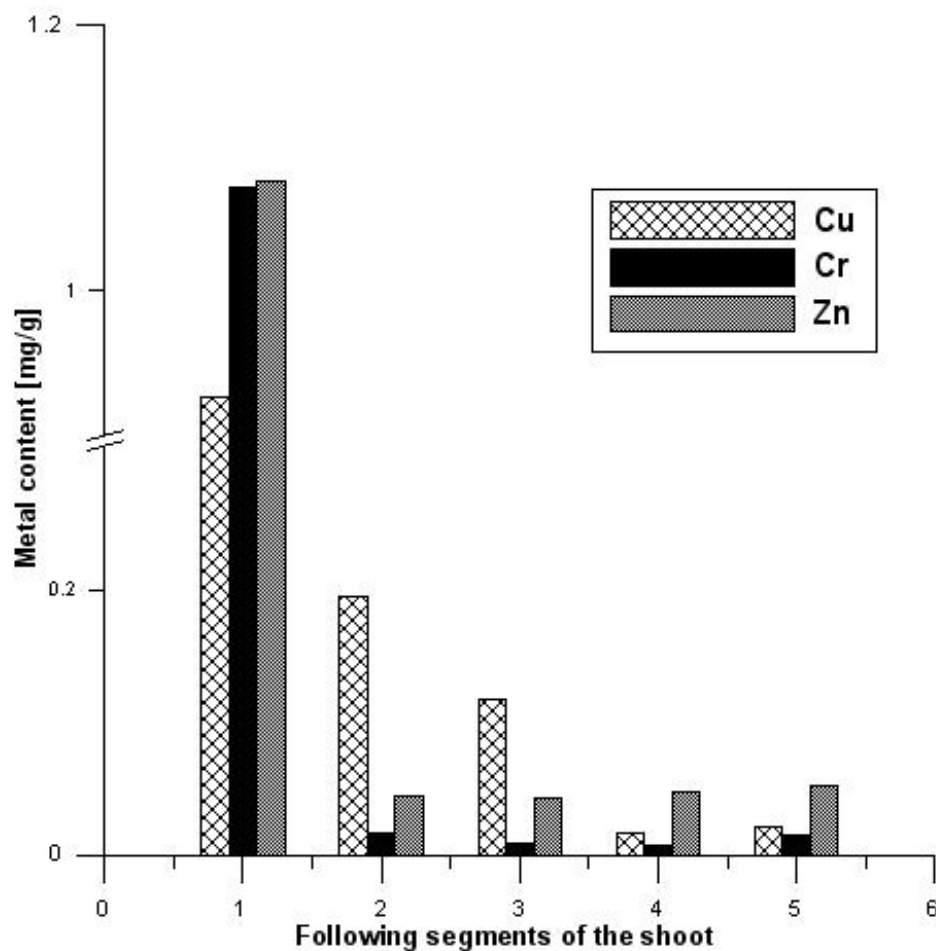


Fig. 2. Metal content in following segments of shoots (distance from rhizosphere: 1.1-5 cm; 2.55-60 cm; 3.110-115 cm; 4.165-170 cm; 5.220-225 cm). (Łukaszewicz et al., 2009).

During the experiment young shoots of *Salix viminalis* after defoliation were put into vessels with water and left until fresh leaves and root sprouted. Selected plants were moved to glass vessels filled with Cu, Cr and Zn salts solutions (0.01 M each). Additionally, chelation agent i. e. EDTA in water solution was added in the amount calculated basing on the assumption that EDTA was capable to form bichelates. According to some authors (Blaylock et al., 1997) plants should be more tolerant to chelated metal ions since after complexation their toxicity is lower. However, there is no common agreement about the positive influence of chelation on the metal ion uptake by *Salix viminalis*. After 7 days the plants were taken form the vessels and appropriate parts of stems (wood samples) were cut and subjected to elemental analysis (fig. 2). It is visible that metal ions enter the aerial part of *Salix viminalis* but the concentration of metals depends on the height above the ground level. Some studies point out differentiated distribution of metal ions in roots, stem, leaves etc. Tables 5 and 6 present such a kind of data (Gąsecka et al., 2010).

| Cu addition [mM/ dm ³] | Cu accumulation (dry weight) [mg/ kg] | | | | Leaves length [cm] | Total leaves surface [cm ²] | Shoots length [cm] | Roots length [cm] | Roots biomass [g] |
|--|--|--------|-------|------|--------------------------|--|--------------------------|-------------------------|-------------------------|
| | Leaves | Shoots | Roots | Rods | | | | | |
| 0 | 0.22 | 0.28 | 0.48 | 1.47 | 6.58 | 194.9 | 9.69 | 9.76 | 11.57 |
| 0.5 | 0.84 | 1.69 | 3.27 | 3.89 | 4.24 | 182.0 | 8.91 | 6.18 | 3.39 |
| 1.0 | 1.65 | 2.46 | 5.38 | 5.25 | 3.97 | 181.3 | 8.77 | 5.69 | 2.66 |
| 1.5 | 2.79 | 2.93 | 8.84 | 6.37 | 3.71 | 179.0 | 8.13 | 4.36 | 2.37 |
| 2.0 | 3.46 | 3.56 | 10.61 | 7.44 | 3.65 | 174.7 | 7.47 | 4.34 | 1.84 |
| 2.5 | 4.22 | 3.90 | 13.51 | 8.17 | 3.42 | 174.6 | 7.55 | 3.99 | 1.82 |
| 3.0 | 4.30 | 4.69 | 15.38 | 9.46 | 3.41 | 171.8 | 5.93 | 3.82 | 0.82 |

Table 5. Copper accumulation in *Salix viminalis* L. organs and biomass parameters for subsequent levels of copper addition to the growing medium – mean values (n=3). Selected data cited after (Gąsecka et al., 2010).

| Tissue | Decreasing metal accumulation abilities of tissues (from left to Wright) | | | | | | |
|---------------|--|----|----|----|----|----|----|
| Root | Zn | Cd | Pb | Cu | Co | Cr | Ni |
| Bark | Cu | Cd | Zn | Co | Pb | Cr | Ni |
| Leaf | Ni | Cr | Co | Zn | Pb | Cu | Cd |
| Petioles | Cd | Cr | Zn | Cu | Pb | Ni | Co |
| Shoot (0.1 m) | Cu | Cr | Zn | Cd | Pb | Ni | Co |
| Shoot (1 m) | Cd | Cr | Cu | Pb | Ni | Zn | Co |

Table 6. Heavy metal accumulation in different tissues of *Salix* materials. The table content cited after (Młeczek et al. 2009) with no changes.

High metal ion accumulation is not an exclusive feature of *Salix viminalis*. Other *Salix* genotypes may exhibit high accumulation capacities towards different heavy metal ions (table 7) with particular emphasis on Zn^{2+} accumulation (Mleczeek et al., 2010).

| <i>Salix</i> genotype | Metal kontent in <i>Salix</i> genotypes [mg / kg] (dry mass) | | | | | | | |
|---|--|------|-------|------|-------|------|------|--------|
| | | Cd | Co | Cr | Cu | Ni | Pb | Zn |
| <i>Salix purpurea</i> var. Angustifolia Kerner | before | 0.86 | 0.134 | 0.67 | 6.54 | 3.05 | 1.93 | 65.72 |
| | after | 1.48 | 0.218 | 0.94 | 7.88 | 8.45 | 2.15 | 70.02 |
| <i>Salix purpurea</i> L. Nigra longifolia pendula | before | 1.64 | 0.112 | 0.99 | 5.72 | 3.08 | 5.62 | 91.46 |
| | after | 1.75 | 0.240 | 1.27 | 6.73 | 9.28 | 6.07 | 96.34 |
| <i>Salix purpurea</i> L. Green Dicks | before | 2.19 | 0.050 | 2.29 | 7.94 | 4.66 | 2.16 | 57.19 |
| | after | 2.47 | 0.098 | 2.51 | 7.98 | 7.49 | 2.51 | 60.86 |
| <i>Salix purpurea</i> L. Uralensis | before | 1.77 | 0.058 | 1.91 | 7.01 | 4.18 | 1.11 | 58.33 |
| | after | 2.42 | 0.122 | 2.32 | 7.49 | 4.86 | 1.39 | 60.65 |
| <i>Salix alba</i> L. Kanon | before | 1.58 | 0.050 | 2.21 | 4.22 | 4.25 | 1.47 | 97.48 |
| | after | 1.87 | 0.095 | 3.04 | 6.47 | 8.44 | 1.53 | 103.21 |
| <i>Salix purpurea</i> var. Schultze Schultze | before | 1.87 | 0.054 | 0.55 | 8.12 | 3.74 | 1.93 | 94.28 |
| | after | 2.03 | 0.124 | 1.02 | 11.51 | 5.46 | 2.29 | 98.33 |
| <i>Salix fragilis</i> L. Kanon | before | 0.89 | 0.057 | 2.02 | 9.35 | 3.51 | 0.97 | 81.48 |
| | after | 1.06 | 0.129 | 2.47 | 10.87 | 7.75 | 1.27 | 84.79 |
| <i>Salix petiolaria</i> Rigida | before | 1.21 | 0.093 | 3.16 | 5.24 | 2.28 | 2.05 | 62.49 |
| | after | 1.58 | 0.174 | 3.78 | 8.89 | 5.46 | 2.40 | 68.92 |
| <i>Salix purpurea</i> 233 | before | 1.57 | 0.026 | 1.61 | 7.13 | 1.97 | 2.88 | 91.37 |
| | after | 1.82 | 0.049 | 2.32 | 10.37 | 3.24 | 3.11 | 98.45 |
| <i>Salix nigra</i> Marsch | before | 0.61 | 0.036 | 0.59 | 8.26 | 6.42 | 1.42 | 102.47 |
| | after | 0.78 | 0.048 | 1.33 | 10.19 | 8.45 | 1.76 | 112.27 |
| <i>Salix japonica</i> | before | 1.51 | 0.069 | 2.74 | 6.79 | 3.68 | 2.07 | 84.25 |
| | after | 1.97 | 0.151 | 3.54 | 8.31 | 7.58 | 2.30 | 89.55 |
| <i>Salix purpurea</i> Utilissima | before | 0.47 | 0.037 | 2.07 | 4.71 | 1.19 | 1.41 | 37.91 |
| | after | 0.92 | 0.059 | 3.18 | 6.95 | 2.73 | 1.76 | 44.51 |

Table 7. Concentration of heavy metals in young shoots of 12 *Salix* genotypes before and after experiment (hydroponic estimation of heavy metal accumulation). Table cited after (Mleczeek et al., 2010) with no changes.

Mechanism of heavy metal intrusion, transportation, deactivation and accumulation has been investigated intensively over many years (Shah & Nongkynrih, 2007; Memon et al., 2001; Lasat, 2001, Clemens, 2006). Fig. 3 illustrates the complex nature of the processes. Shah & Nongkynrih, 2007 recall several basic mechanism of metal ion assimilation among which chelating plays a crucial role. Many substances (chelators) occurring in plant cells contain typical chelating (ligand) atoms like oxygen, nitrogen and sulfur ones. Chelators contribute to metal ion detoxification. Other functional compounds called chaperones specifically deliver metal ions to organelles and metalrequiring. The principal metal chelators in plants are phytochelatins, metallothioneins, organic acids and amino acids. Shah & Nongkynrih, 2007 after some other authors state that phytochelatins are small metal-binding peptides which formation involves glutathione, homogluthathione, hydroxymethyl-gluthathione or gamma-glutamylcysteine. Metallothioneins are low molecular mass cysteine (cys)-rich proteins, that

bind metal ions in metal-thiolate clusters. Over 50 metallothioneins has been identified so far in plants. Organic acids and amino acids because of N and O content may chelate intensively various metal ions. Shah & Nongkynrih, 2007 claim that “citrate, malate, and oxalate have been implicated in a range of processes, including differential metal tolerance, metal transport through xylem and vacuolar metal sequestration”. Salicylic acid and its derivatives which are definitely present in *Salix viminalis* tissues, has been also identified as chelating agent in some plants. For *Salix viminalis* naturally high concentration of the latter species is probably the key factor providing hyperaccumulating properties of the plant.

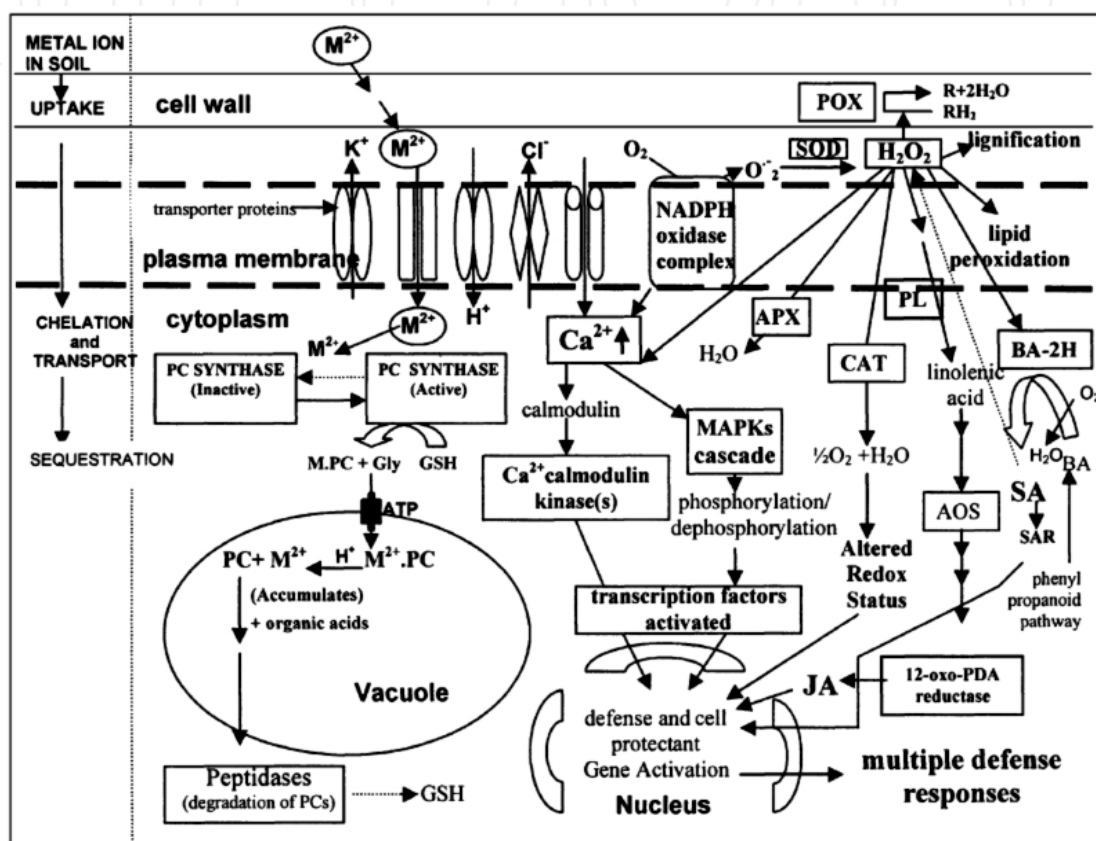


Fig. 3. A model of the mechanisms that occur in plant cell upon exposure to metals: metal ion uptake, chelation, transport, sequestration, signalling and signal transduction. The diagram shows the uptake of metal ions by K^+ efflux and transporter proteins, their sequestration by formation of PCs by enzyme PC synthase and GSH in vacuoles, the subsequent degradation of PC-peptides by peptidases to release GSH, the generation of ROI species, the contribution of Ca^{2+} towards activation of Ca^{2+} /calmodulin kinase(s) and MAP kinase(s) cascade leading to defense gene activation in nucleus, the effect of ROI on natural plant defense pathways like octadecanoid pathway (JA) and phenyl propanoid pathway (SA) biosynthesis that lead to defense and cell protectant gene activation is also included to correlate the induced metal stress defense with natural plant defense mechanism. AOS - allene oxide synthase; APX - ascorbate peroxidase; BA - benzoic acid; BA-2H - benzoic acid 2-hydroxylase; CAT - catalase; GSH - glutathione; JA - jasmonic acid; M^{2+} - metal ions; MAPK - mitogen activated protein kinase; 12-oxo PDA reductase - 12-oxo-cis-10,15-phytodienoic acid reductase; PC - phytochelatins; PL - phospholipase; POX - peroxidase; SA - salicylic acid; SOD - superoxide dismutase. The figure and the caption cited with no changes after Shah & Nongkynrih, 2007.

Memon et al., claim that the application of biological metal-accumulators and metal-hyperaccumulators for purification of soils and waters has several positive features like “low cost, generation of a recyclable metal-rich plant residue, applicability to a range of toxic metals and radionuclides, minimal environmental disturbance, elimination of secondary air or water-borne wastes, and public acceptance”. The latter statement applies in full to *Salix viminalis*, too. Table 8 proves that Cd removal from soil is extraordinarily high (217 g/ha) if compared to other phytoaccumulators tested in the study (Porębska & Ostrowska, 1999). Also the concentration of the metal in dry *Salix viminalis* wood was very high (22.1 mg/kg) exceeding values found in our study Łukaszewicz et al., 2009.

| Plant | Biomass [t / ha] | Metal content [mg / kg] (dry weight) | Metal removal [g / ha] |
|-----------------------------|------------------|--------------------------------------|------------------------|
| <i>Thlaspi caerulescens</i> | 2.93 | 12.1 | 35 |
| <i>Alyssum murale</i> | 1.32 | 33.7 | 43 |
| <i>Salix viminalis</i> | 10.00 | 22.1 | 217 |
| Potato - tuber | 14.77 | 3.2 | 47 |
| Barley - straw | 4.95 | 2.4 | 12 |
| Barley - grain | 3.14 | 0.70 | 2 |
| White clover | 3.52 | 1.14 | 4 |

Table 8. Estimated removal of Cd with the biomass. Selected data cited and translated after Porębska & Ostrowska, 2009.

3. Unconventional application of *Salix viminalis*

3.1 Fabrication of adsorbents and catalysts

The above described proved efficiency in metal ion accumulation by *Salix viminalis* led to a novel concept of non-energetic use of the plant. In some earlier studies (Łukaszewicz & Wesółowski, 2008) authors have discovered that thermal treatment (oxygen free conditions) of dry *Salix viminalis* wood yields charcoals of a very original and potentially useful pore structure. Usually a two step procedure was applied:

- 1 hour long preliminary carbonization in an inert gas atmosphere at 600 °C,
- 1 hour long secondary carbonization in an inert gas atmosphere at a desired temperature ranging from 600 to 900 °C.

The pore structure of such obtained charcoals is characteristic because of a very narrow pore size distribution function (PSD) i. e. only pores of not differentiated dimensions contribute to the total pore volume (figs 4, 5 and 6). The calculated dimensions of pores let to call such fabricated charcoals “nanoporous Carbon Molecular Sieves” (CMS).

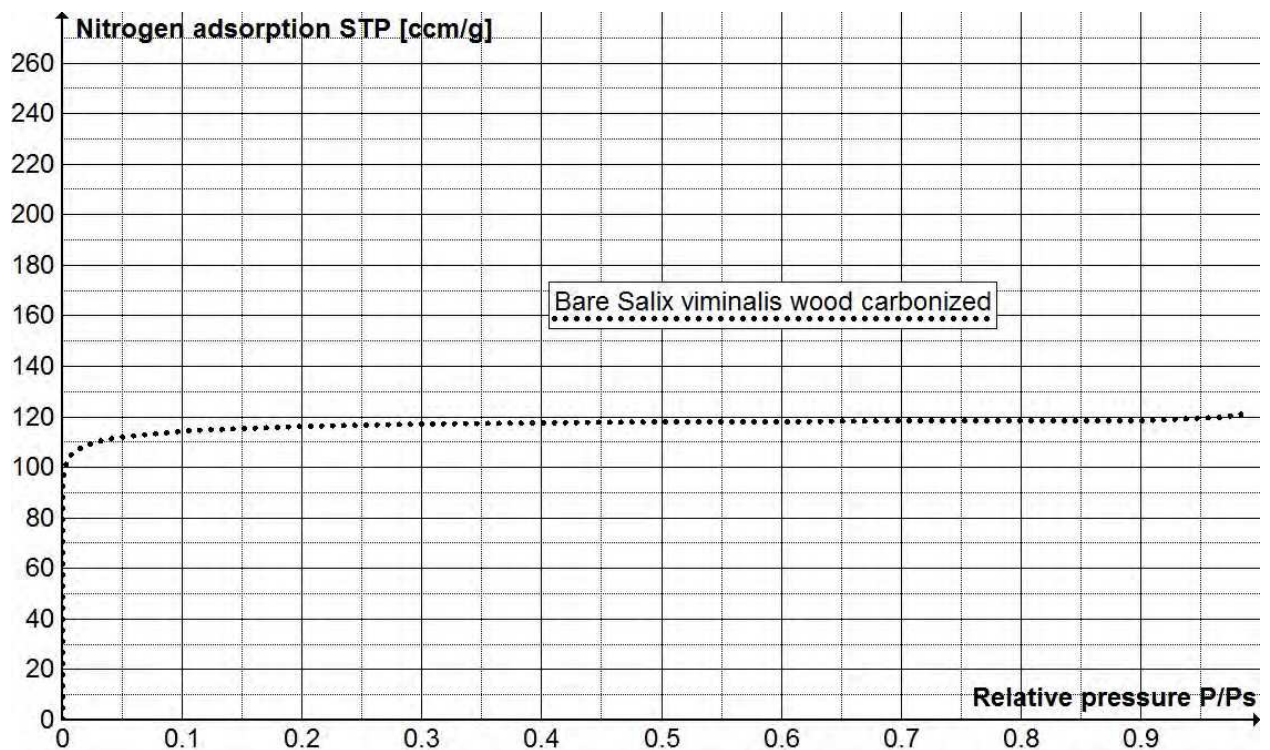


Fig. 4. Nitrogen adsorption isotherm at $-196\text{ }^{\circ}\text{C}$ for bare *Salix viminalis* wood finally carbonized at $700\text{ }^{\circ}\text{C}$. I type isotherm characteristic for the presence of nanopores.

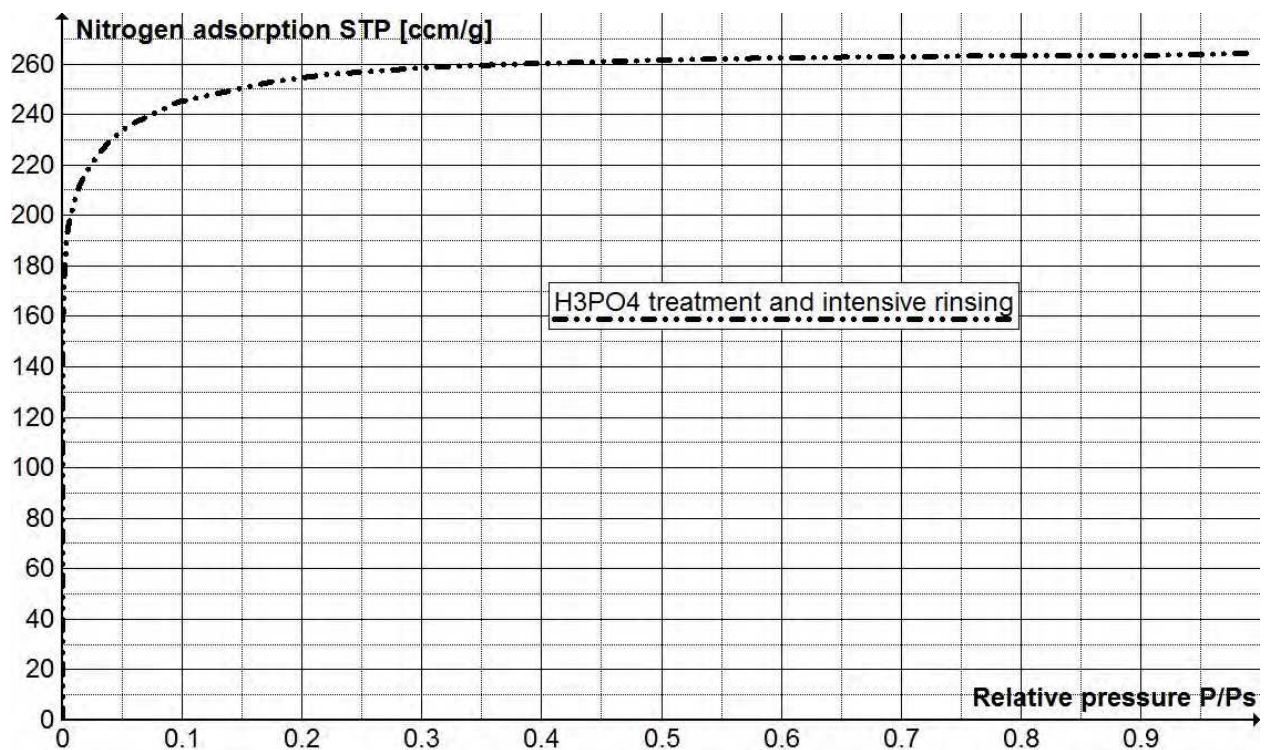


Fig. 5. Nitrogen adsorption isotherm at $-196\text{ }^{\circ}\text{C}$ for activated *Salix viminalis* wood (phosphoric acid treatment) finally carbonized at $700\text{ }^{\circ}\text{C}$. I type isotherm characteristic for the presence of nanopores.

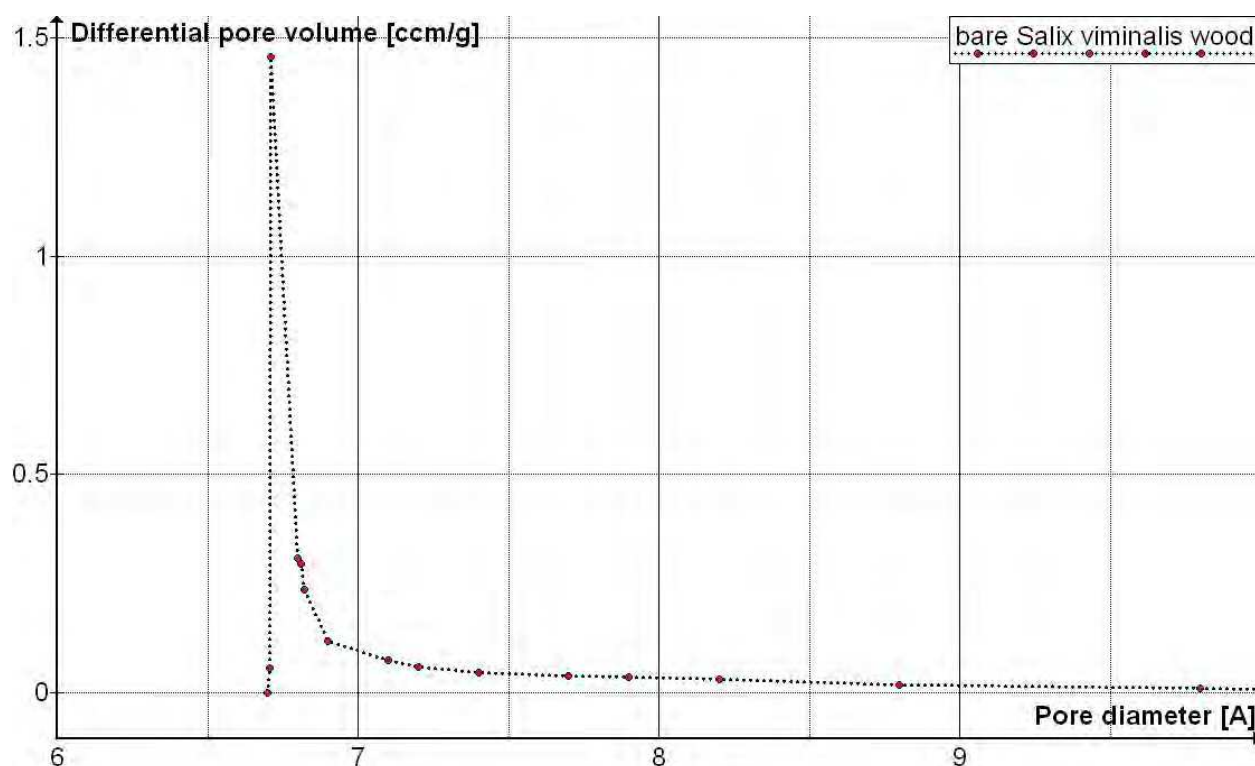


Fig. 6. Pore size distribution function (PSD) determined from low temperature (-196°C) nitrogen adsorption data by means of Horvath-Kawazoe method (Horvath & Kawazoe, 1983).

The *Salix viminalis* originated CMSs proved their sieving properties in gas mixture separation to single components in chromatographic conditions (Gorska, 2009). For example table 9 contains separation coefficients determined for N_2/CH_4 binary gas mixture over two example *Salix viminalis* originated CMSs of similar surface area. The separation is of industrial importance since natural gas resources are often contaminated by nitrogen which high content may reduce commercial value of methane. The values are dramatically bigger than 1 at all investigated temperatures i. e. 30, 40, 50, 60 and 70°C . It is to emphasize that separation is very efficient at highest temperature of 70°C . It is particularly important regarding a potential application of such carbons as and adsorbing bed in a PSA (Pressure Swing Adsorption) installation. In the PSA method, the first step consists in the compression of a gas mixture to be separated in the adsorbing chamber (filled with CMS). Gas compression is an exothermal process leading to the warming of gases and carbon adsorbent what is an undesired phenomenon since separation at high temperature is generally much worse since PSA separation of air is very temperature sensitive (Japan EnviroChemicals Ltd., 2011).

The described fabrication of CMSs does not exploit both unique features of *Salix viminalis* i. e. the unique ability of *Salix viminalis* biomass transformation into a CMS and the *Salix viminalis* ability to heavy metal ion accumulation. Both feature were exploited in the case of a series of hybrid carbon-metal oxide catalysts obtained according to the fabrication procedure proposed recently by Łukaszewicz et al., 2007. The novelty of the method consists in the exploitation of natural phenomenon of metal ion transportation in living plants for the introduction of a metal-based catalytic phase. Metal ions, after introduction to transport-responsible tissues in a living plant (*Salix viminalis*), are transported to the plant cells. The process was efficient since *Salix viminalis* was highly tolerant to the presence of heavy metal ions in its body. Freshly cut ca. 20 cm long sections of a stem (rootless) of *Salix viminalis* were immersed (vertical alignment) in a water solution containing equimolar quantities of $\text{La}(\text{NO}_3)_3$ and $\text{Mn}(\text{NO}_3)_2$ (example concentrations: 0.001M, 0.01M, 0.1M). The stems were fresh enough to preserve intensive metal ion transport resulting in a gradual rise of the solution along the treated stems. A contrast dye was added to the solutions in some experiments to provide eye observation of the capillary rise of solutions along the treated stems. On the other hand, the length of stems was short enough to avoid differentiated distribution of metal ions in the stem what might be expected regarding some former tests (see figs 1 and 2). After the contact with La^{3+} and Mn^{2+} ion solutions, the metal saturated stems were dried, diminished and carbonized (600-800 °C, a two-step procedure) in an inert gas atmosphere (N_2). The first carbonization let to expel volatile species and to transform the wood (lignin-cellulose matrix) into carbon matrix (CMS resembling), consisting mainly of C, O, N and H atoms (Gorska, 2009). The next heat treatment (1 h, N_2 flow) at the temperature of 800 °C did not destroy already developed pore structure (preliminary carbonization) and, what is the most important, it enabled the transformation of introduced metal ions into the corresponding metal clusters. XPS and XRD analysis (Cyganiuk et al., 2010) proved that a complex oxide LaMnO_3 was synthesized from introduced ions. SEM and HRTEM investigations proved that the provskite-type oxide is present in such obtained samples in form of inorganic nano-crystallites suspended in carbon matrix, which in general was an amorphous material with few graphite nano-crystallites (figs 7 and 8).

| Temp [°C] | Carbon 1 [$S_{\text{BET}} = 312 \pm 9.5 \text{ m}^2/\text{g}$] | | Carbon 2 [$S_{\text{BET}} = 358 \pm 10.94 \text{ m}^2/\text{g}$] | |
|-----------|--|-----------------------|--|-----------------------|
| | Rs | $\pm \Delta\text{Rs}$ | Rs | $\pm \Delta\text{Rs}$ |
| 70 | 3.64 | 0.31 | 4.80 | 0.75 |
| 60 | 3.55 | 0.24 | 4.71 | 0.26 |
| 50 | 3.74 | 0.62 | 4.91 | 0.19 |
| 40 | 3.83 | 0.53 | 5.25 | 3.52 |
| 30 | 4.17 | 0.34 | 5.87 | 0.01 |

Table 9. Separation factors determined the separation of N_2/CH_4 binary gas mixtures. Separating medium – *Salix viminalis* originated carbons. Specific surface area S_{BET} determined by BET method from low temperature (-196 °C) nitrogen adsorption. Calculated from data collected by Gorska, 2009.

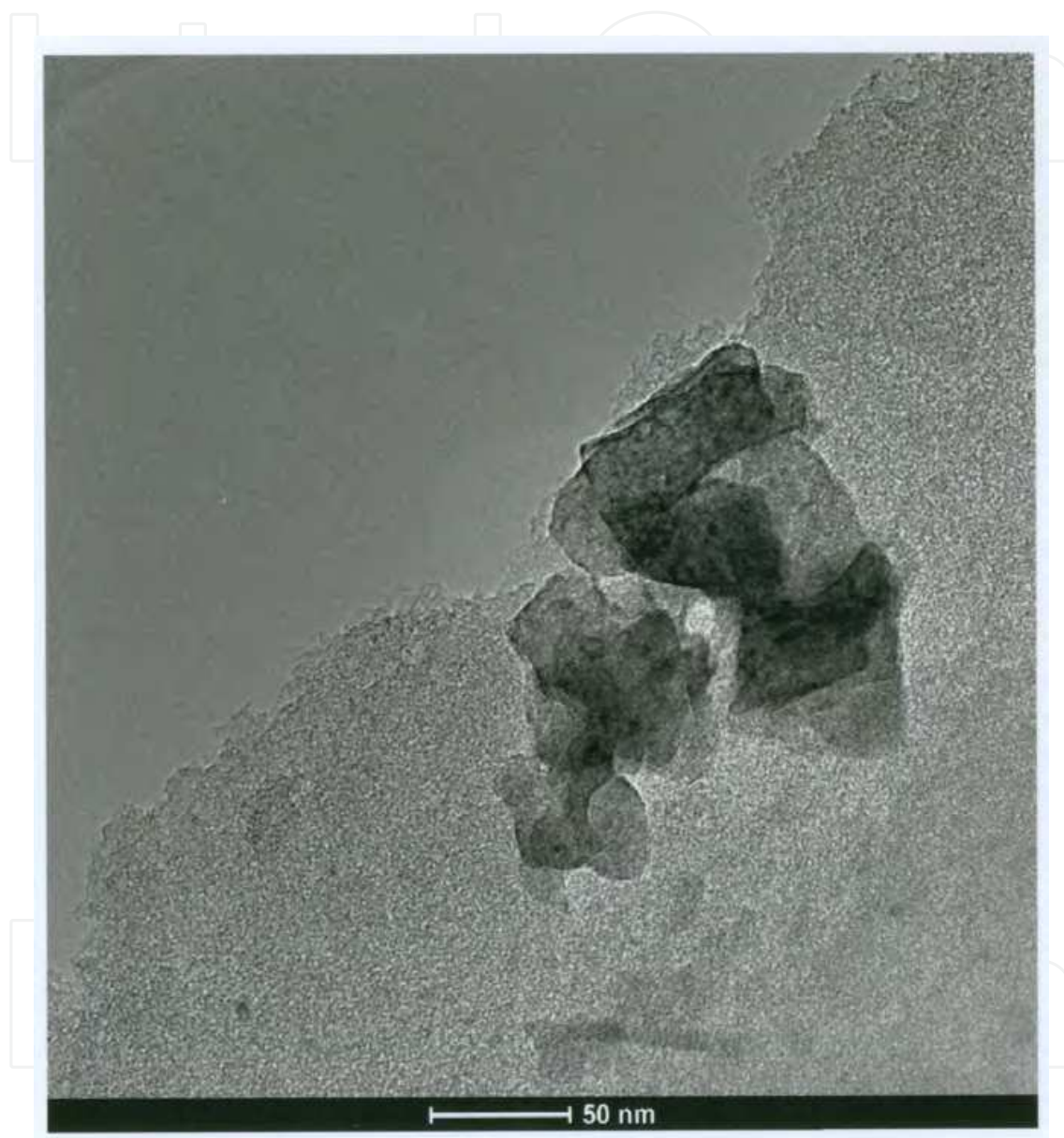


Fig. 7. HRTEM image of a LaMnO₃ crystallite embedded in the carbon matrix.

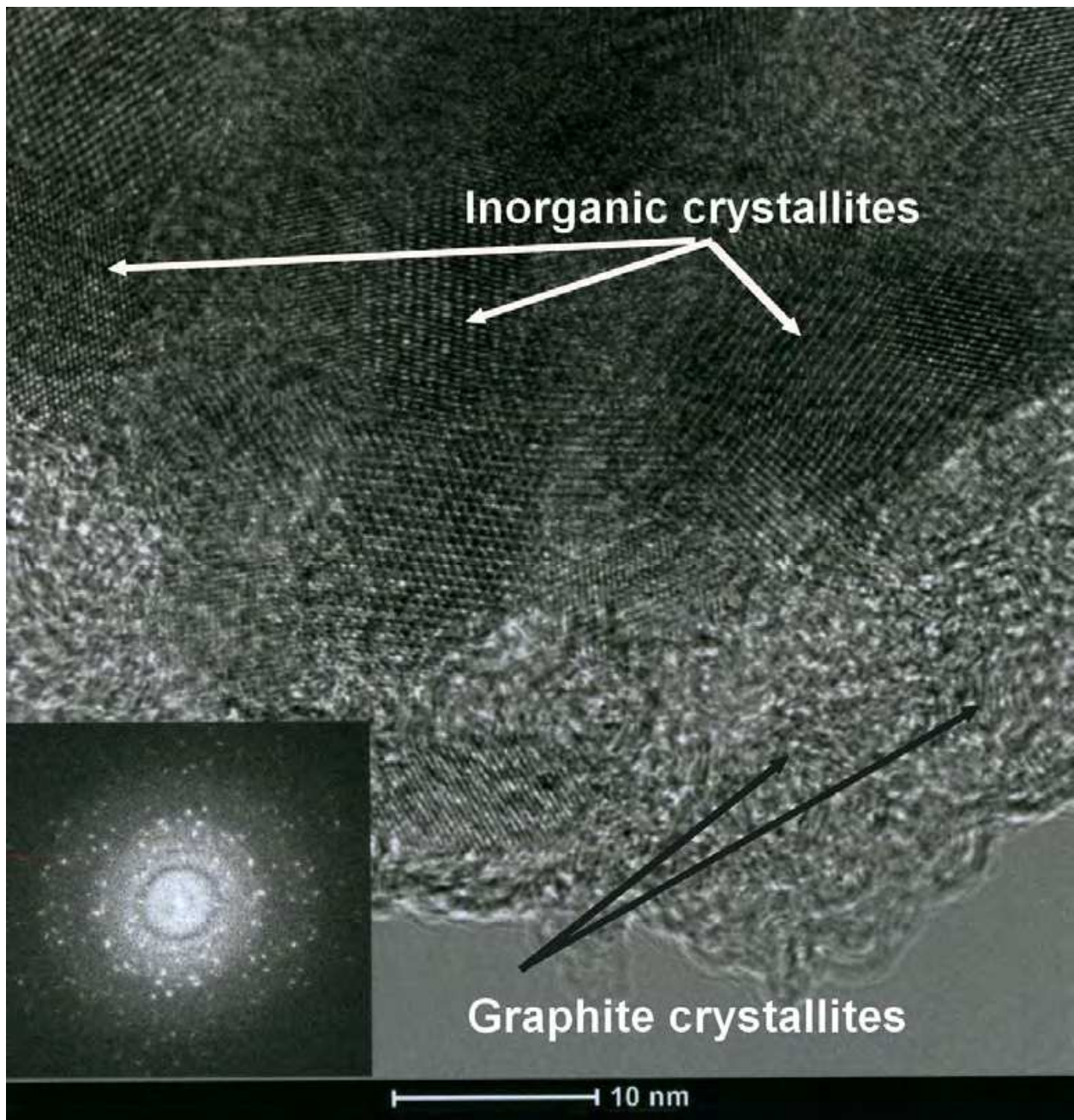


Fig. 8. HRTEM image of a LaMnO_3 crystallite embedded in the carbon matrix. Crystalline domains (graphite crystallites) visible in the amorphous carbon matrix.

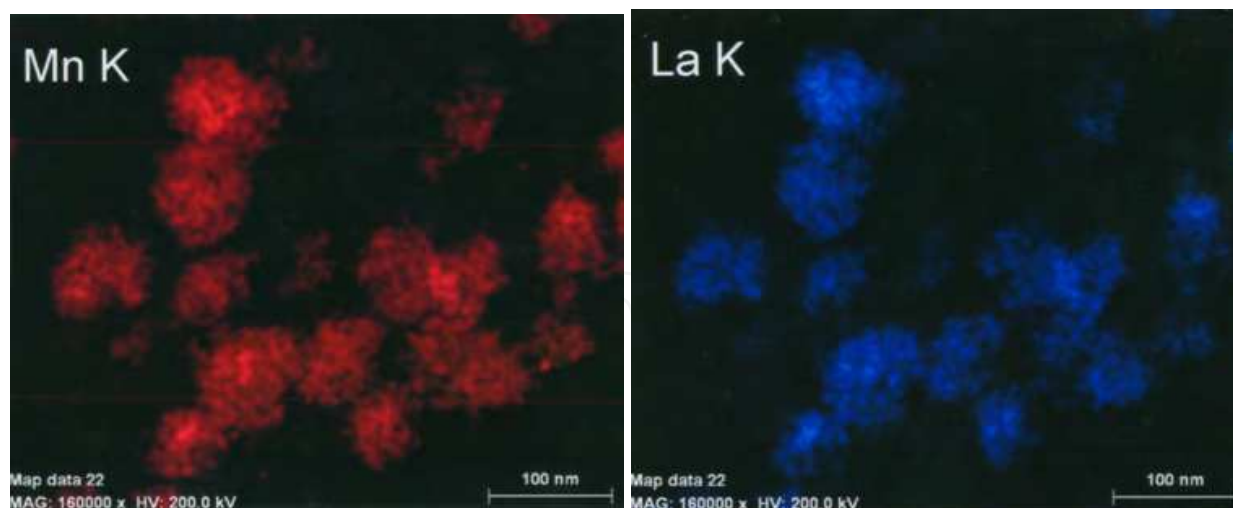


Fig. 9. Identical distribution of Mn (left) and La (right) atoms in hybrid C/LaMnO₃ catalyst.

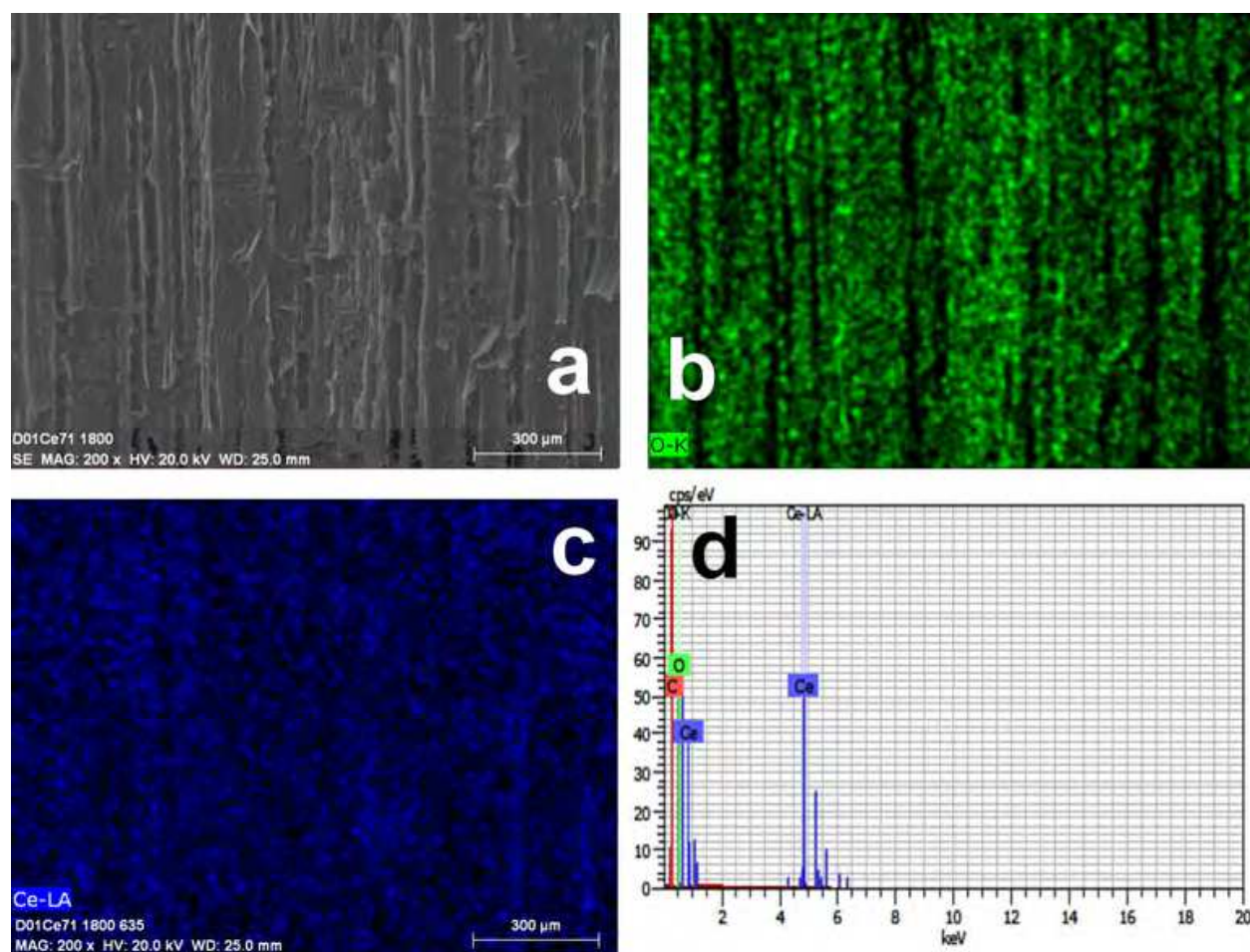


Fig. 10. SEM and SEM-EDS/EDX analysis of hybrid C/Ce catalysts obtained from *Salix viminalis*: a – SEM micrograph, b – distribution of oxygen atoms determined by SEM-EDS/EDX, c – distribution of cerium atoms determined by SEM-EDS/EDX, d – elemental analysis of the hybrid material.

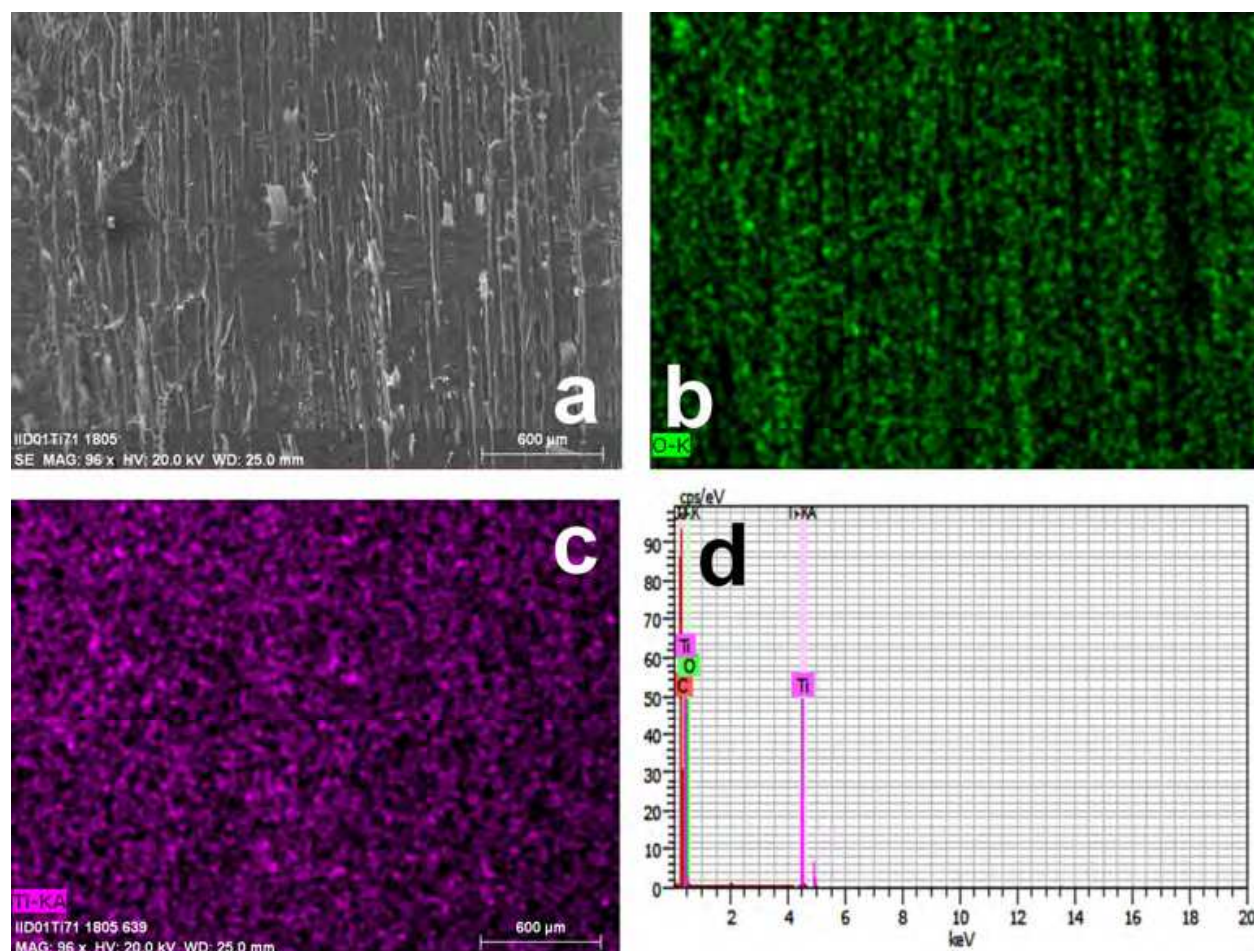


Fig. 11. SEM and SEM-EDS/EDX analysis of hybrid C/Ti catalysts obtained from *Salix viminalis*: a – SEM micrograph, b – distribution of oxygen atoms determined by SEM-EDS/EDX, c – distribution of titanium atoms determined by SEM-EDS/EDX, d – elemental analysis of the hybrid material.

Such obtained hybrid materials were tested as catalysts for n-butanol conversion to a 4-heptanone according to the reaction:



The catalysts exhibited very good catalytic performance despite very low concentration of the active component i. e. a perovskite-type oxide LaMnO_3 (atomic content below 1%). The noticed high activity i. e. yield and selectivity (Cyganiuk et al., 2010) resulted from very high dispersion of the active phase understood as:

- - reduced size of LaMnO_3 crystallites (10-100 nm),
- - uniform distribution of both metals in the carbon matrix (fig. 9).

Similarly, titanium and cerium based hybrid materials were obtained by exploitation of metal ion transportation in living parts of *Salix viminalis* (ca. 20 cm long stem sections). Figs 10 and 11 depict uniform distribution of Ce and Ti atoms in a carbon matrixes. Their occurrence is accompanied by oxygen atoms however the latter are a usual constituent of carbon matrixes and can not be exclusively associated with Ce and Ti in the form of metal oxides. Elemental analysis data definitely prove (figs 10 and 11) that Ce and Ti are present in investigated hybrid

samples and their presence result only from the performed fabrication procedure. The elements are relatively rare and have not been found in the samples of non-impregnated but carbonized *Salix viminalis* wood. Also in this case the atomic content of the metals is very low i. e. definitely below 1% despite of the concentration of impregnating solution. Thus, the proposed exploitation of metal ion transport in living parts of *Salix viminalis* ensures rather low level of impregnation but of very high dispersion. The Ti and Ce containing hybrid materials were tested as catalysts, too. Both materials despite of the same properties of carbon component of them, exhibited dramatically different catalytic activity:

- Ti/C hybrids towards dehydration of n-alcohols (n-butanol conversion to butane, ca. 55% selectivity at 460 °C),
- Ce/C hybrids towards ketonization of n-alcohols (n-butanol conversion to heptanone-4, ca. 75% selectivity at 460 °C).

The differences must be attributed to different catalytic properties of the active components of the hybrid materials i. e. to Ce and Ti derivatives (mixed oxides) which presence was proved by XRD, XPS and HRTEM measurements.

In summary, the proposed hybrid catalysts fabrication method is basing on two important and exclusive features of *Salix viminalis*:

- high vitality preserving some living functions like metal ion transportation in fragments of a complete plant (single rod cut into 20 cm long pieces),
- high tolerance of still living parts of *Salix viminalis* to heavy metal ions which enter the plant structure. We assume that toxic influence of the heavy metal ions is considerably reduced in the plant cells otherwise transportation of metal ions could be severely disrupted and finally terminated. During impregnation in most *Salix viminalis* samples (sections of rod) no visible morphological changes were observed and the 20 cm long sections retained their original olive-green color characteristic for its bark. Visible bulge and shrinkage did not occur.

The originality of the above presented concept let to submit patent applications (Łukaszewicz et al., 2006; Łukaszewicz et al., 2007).

3.2 Dry distillation of *Salix viminalis* wood

Fabrication of charcoals from *Salix viminalis* consists in the a heat treatment of the biomass in oxygen free conditions. In fact this process can be also called dry distillation w wood. However, usually distillation is run aiming at the collection of volatile products which evolve during heat treatment. Looking at charcoal fabrication (described above) from such a point view authors has decided to cool down (liquefaction) volatiles leaving heating zone of stove along with the stream of inert gas (nitrogen) passing through the stove. The condensate in form of a dark brown viscous liquid was collected in a glass beaker and subsequently subjected to several analysis. We assumed that the condensate is a mixture of numerous organic compound as in the case of wood tar obtained by dry distillation of other sorts of wood i. e. pine (Egenberg et al., 2002).

At the beginning we assumed that the collected tar must contain phenols and polyphenols which are created during thermolysis of lignin (de Wild et al., 2010). *Salix viminalis* wood contains ca. 20-24 % (by weight) of lignin in dry mass of wood (Mleczek et al., 2010). The distillate called biooil was subjected to some separation measures like extraction to isolate several fractions containing polyphenols. Polyphenols are a precious group of compounds mainly because of their antioxidant properties.

3.3 Polyphenols and other antioxidants

Free radicals play important role in the functioning of human organism (Grajek, 2007). However, their presence may be the reason of oxidative stress. The stress often results from disrupted balance between peroxidants and antioxidants in an organism. It is proven that high activity of free radicals and prolonged influence of oxidative stress are responsible for pathogenesis of nearly 100 diseases (Wolski, 2007) including Alzheimer and Parkinson diseases (Bartosz, 2008; Fitak & Grzegorzczak-Jaźwińska, 1999). During ageing oxidative damages in cells become more frequent with parallel reduction the activity of antioxidative enzymes. The situation becomes worse due to UV irradiation, environmental pollution, permanent mental stress and bad nutrition habits. Oxygen being the base of human existence is mainly available in its triplet form O_2^{*} . The electron configuration results in moderate chemical activity in contrast to other forms like (O_2^{*-}) , HO_2^{*} and OH^{*} . The latter form is considered as the most reactive. Proper enzymes ensure control over 98-99% of all oxygen in a human body. However, the remaining amount of oxygen may undergo transformation (Fenton reaction, Haber-Weiss reaction) into the most reactive forms i. e. oxygen derivatives being free radicals. Daily up to 10 thousand DNA oxygen-related damages occur in a human body. The damages may be repaired by some specific enzymes but the introduction of antioxidants should reduce the threat. Therefore everyday diet has to be supplemented by natural antioxidants. Antioxidation properties of polyphenols may involve the three general mechanisms:

- direct expunge of reactive form of oxygen and nitrogen by two possible pathways: Single Electron Transfer (SET) or Hydrogen Atom Transfer (HAT). In such processes a polyphenol molecule transforms into a phenoxyl radical which after reaction with a next oxygen radical stabilizes as quinone like structure (fig. 12)
- chelation of transition metal ions (particularly copper and iron) which participate in the reactions leading to the formation of reactive radicals like the Fenton reaction involving Fe^{2+} ions and yielding dangerous hydroxyl radical OH ,
- increasing of concentration of endogenous antioxidants and/or inhibition of enzymes stimulating the formation of free radicals.

Such positive chemical features of polyphenols turns peoples attention towards intensive search for sources of them and the development of methods of polyphenols separation from their natural matrixes for further enrichment of some products like pharmaceuticals, food, cosmetics etc. This way of thinking involves investigations on appropriate plants i. e. candidates for a subsequent chemical treatment like polyphenol extraction. According to some extended studies (Makowska-Wąs & Janeczko, 2004) polyphenols occur in many plants and plant originated products like herbs, needles of coniferous plants, algae, green tea leaves, eucalyptus wood, byproducts of olive, wine, yeast production. It is obvious that chemical exploitation of one source plant yields a limited number of polyphenols and search for other polyphenols needs a selection and a proper treatment of another source plants. It has to be stated that the polyphenol content in source plants is very differentiated but also very low. Table 10 informs about the antioxidant activity determined for 100 g of example fruits and vegetables. The highest activity is noticed for pure vitamins and synthetic antioxidants. However, the mentioned products owe their antioxidative activity not only due to the presence of polyphenols since other type of antioxidants may be present, too.

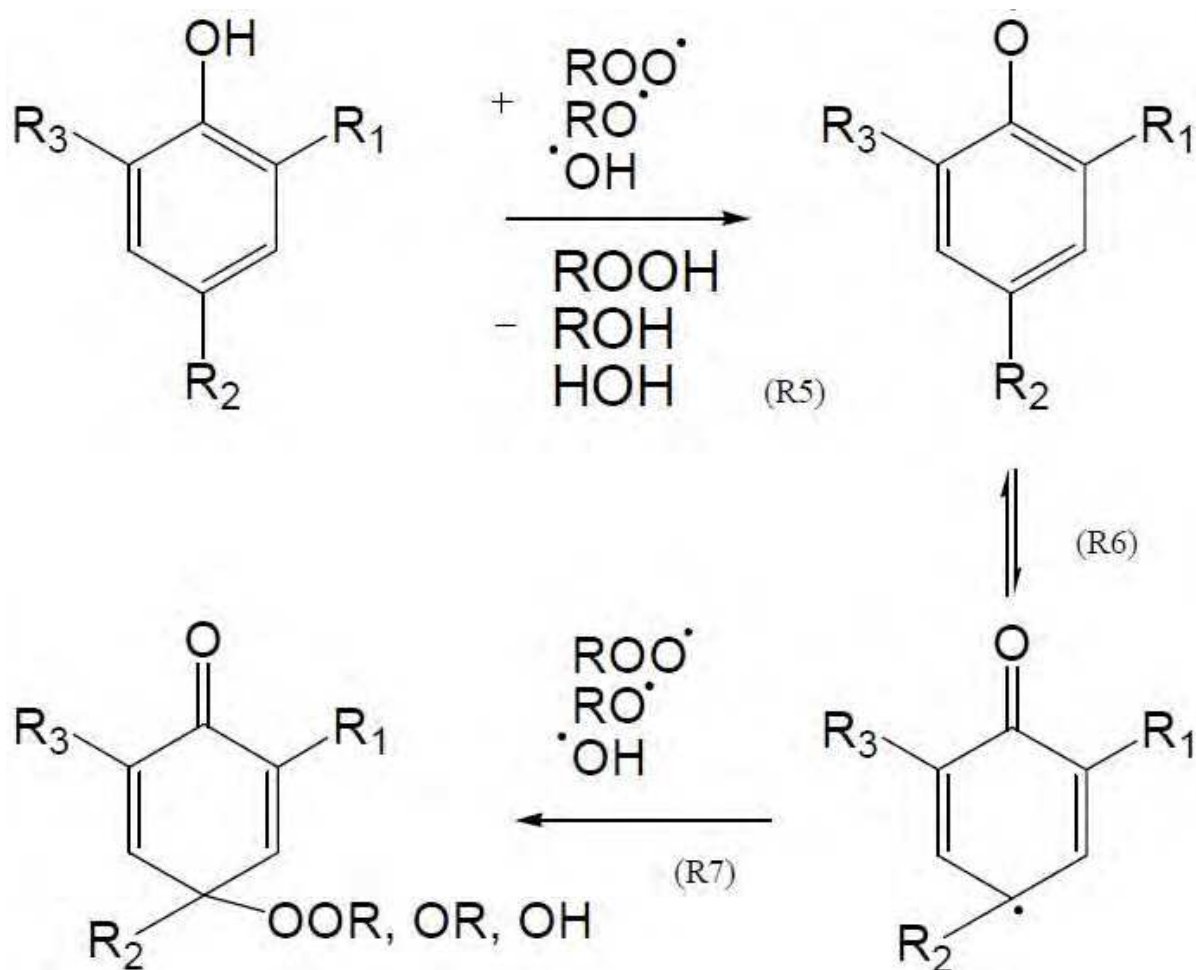


Fig. 12. Oxygen based free radical reaction with a polyphenol.

Obviously the above list is not closed and other natural and synthetic products may be added and therefore search for other effective products is fully justified. Authors' attention has turned towards chemical processing of some easily accessible and renewable resources. Our primary idea was to involve chemical processing not limited to the separation of already existing polyphenols (a passive approach) but also on treatments that transform original matter of low polyphenol content into a new product of high polyphenol concentration (active approach). Such a concept focused our attention on *Salix viminalis* again due to its inexpensiveness, renewable cultivation and high content of lignin which thermal treatment releases polyphenols. As the matter of fact *Salix viminalis* as a living plant contains some amounts of different polyphenols like flavonoids (flavanols, flavones, flavonones, flavonone dimers, chalcones), phenolic acids, lignans, catechin and its derivatives as well as tannins (procyanidins, prodelphinidins) being derivatives of flavan-3-ols. Particular *Salix* species differ much regarding the total content of polyphenols (Nyman & Julkunen-Tiitto, 2005) and their type (Landucci et al., 2003).

For example *Salix caprea* contains a variety of flavonoids and the lack of lignans (Pohjamo et al., 2002). Contrastly, for *Salix viminalis* characteristic are relatively low concentrations of flavonoids (Harborne & Baxter, 1999), moderate concentrations of lignans (Pohjamo et al., 2003) and high concentrations of tannins (Nikitina & Orazov, 2001).

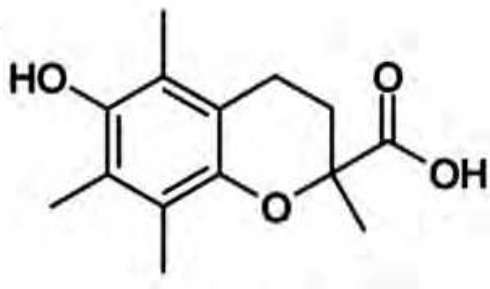
| Food produkt | Antioxidant activity [TE/100 g] |
|------------------------|--|
| Red Grapes | 1350 |
| Red Cabbage | 1000 |
| Broccoli Flowers | 500 |
| Spinach | 500 |
| Green Grapes | 400 |
| Tomato | 300 |
| Green Beans | 175 |
| Green Cabbage | 150 |
| Lima Beans | 1055 |
| Red Beans | 11459 |
| Blueberries | 3300 |
| Raisins | 5900 |
| Wheat Bran | 4620 |
| Wheat Flour (refined) | 600 |
| Substance | Antioxidant activity [TE/100 g] |
| Ascorbate | 442 000 |
| Trilox | 400 000 |
| Witamin E | 201 000 |
| BHT | 395 000 |
| TE - TRILOX Equivalent |  <p>TRILOX</p> |

Table 10. Antioxidant activity of selected food products, vitamins and synthetic antioxidants. Selected points cited after (Prakash et al., 2010).

The concentration of polyphenols in *Salix viminalis* depends also on the season of the year. The maximal concentration of flavonoids is reached during blossom while tannins concentration is highest in Autumn (Nikitina & Orazov, 2001). Long exposure of *Salix viminalis* to sunshine (UV radiation) additionally increases the content of compounds capable to neutralization of free radicals (flavonoids, phenolic acids, proanthocyanidynes) and reduces the content of salicylic acid and its derivatives (Tegelberg & Julkunen-Titto, 2001). Thus, a proper cultivation of *Salix viminalis* and well planned collection of polyphenols by extractive methods may result in a better efficiency of the whole attempt. However, as mentioned earlier, the total contents of polyphenols is relatively low and therefore the mass of isolated antioxidants in relation to the mass of raw material is dramatically low. Thus, the contemporary chemical technology should not only rely on the Nature's productivity but also search for more effective methods of polyphenols fabrication instead of collection. The heat-treatment of *Salix viminalis* wood yields three basic products (charcoal, biooil, biogas) but yield of each depends on heating rate as depicted in fig. 13).

As mentioned biooil formation is a result of lignin pyrolysis. Lignin is biopolymer (fig. 14) consisting of some characteristic units i. e. p-cumarol alcohol, coniferyl alcohol, synapine alcohol (fig. 15.) bonded by various organic bridges. Thus, the bonds may break at different point yielding a huge number of organic compounds including polyphenols. Volatile products evolve during heat-treatment with unequal intensity (fig. 16). The most intensive collection of liquid condensate is possible in the temperature range of 260-380 °C).

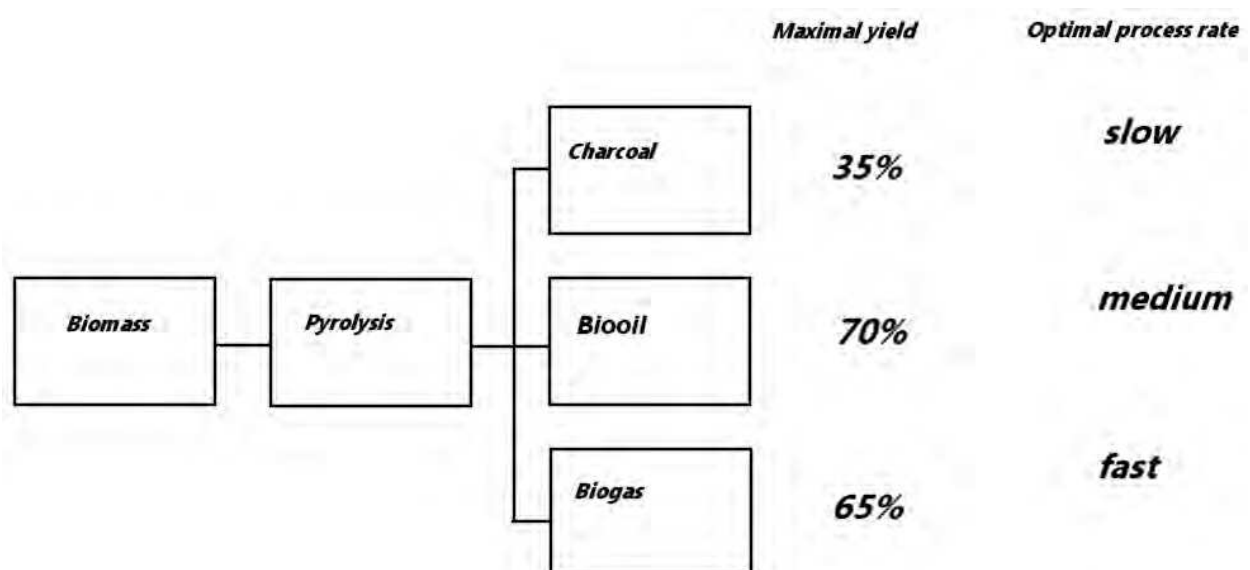


Fig. 13. Typical products of biomass pyrolysis. The influence of process conditions (heating rate, temperature) on yield of particular products.

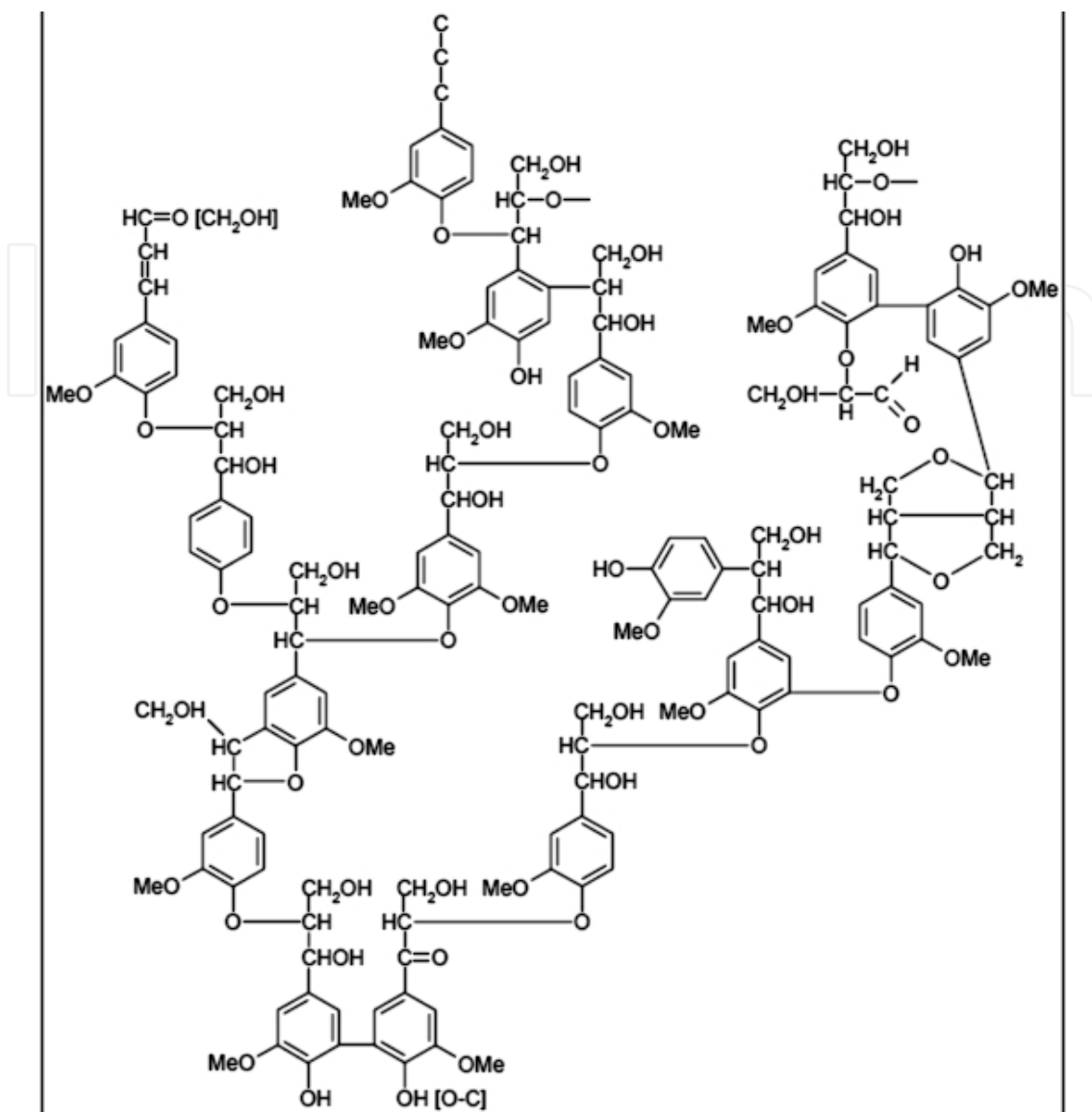


Fig. 14. Pattern structure of lignin.

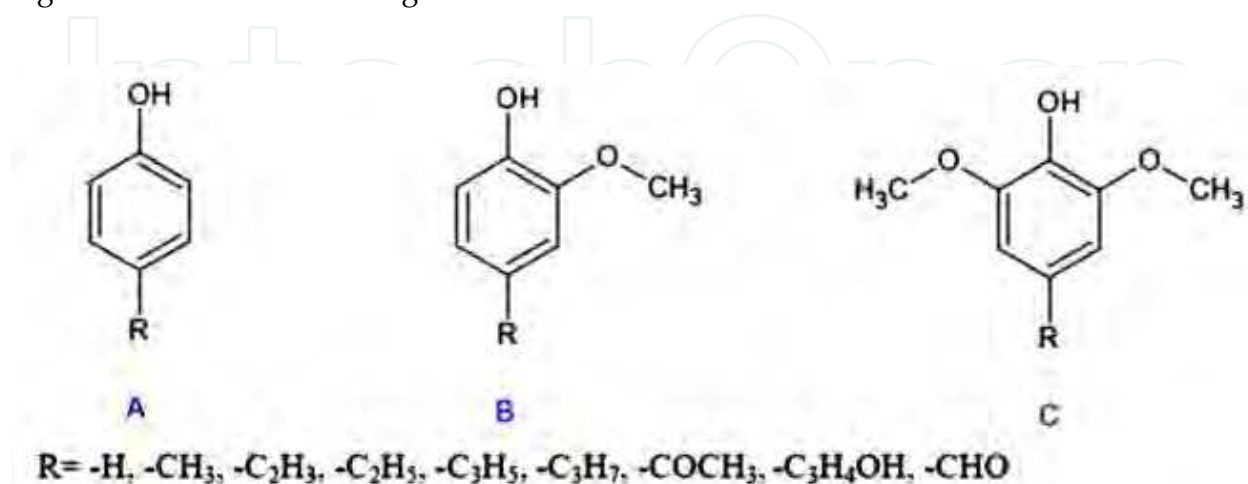


Fig. 15. Structures of three phenolic alcohols being monomers in lignin: A – p-cumarol alcohol, B – coniferyl alcohol, C – synapine alcohol.

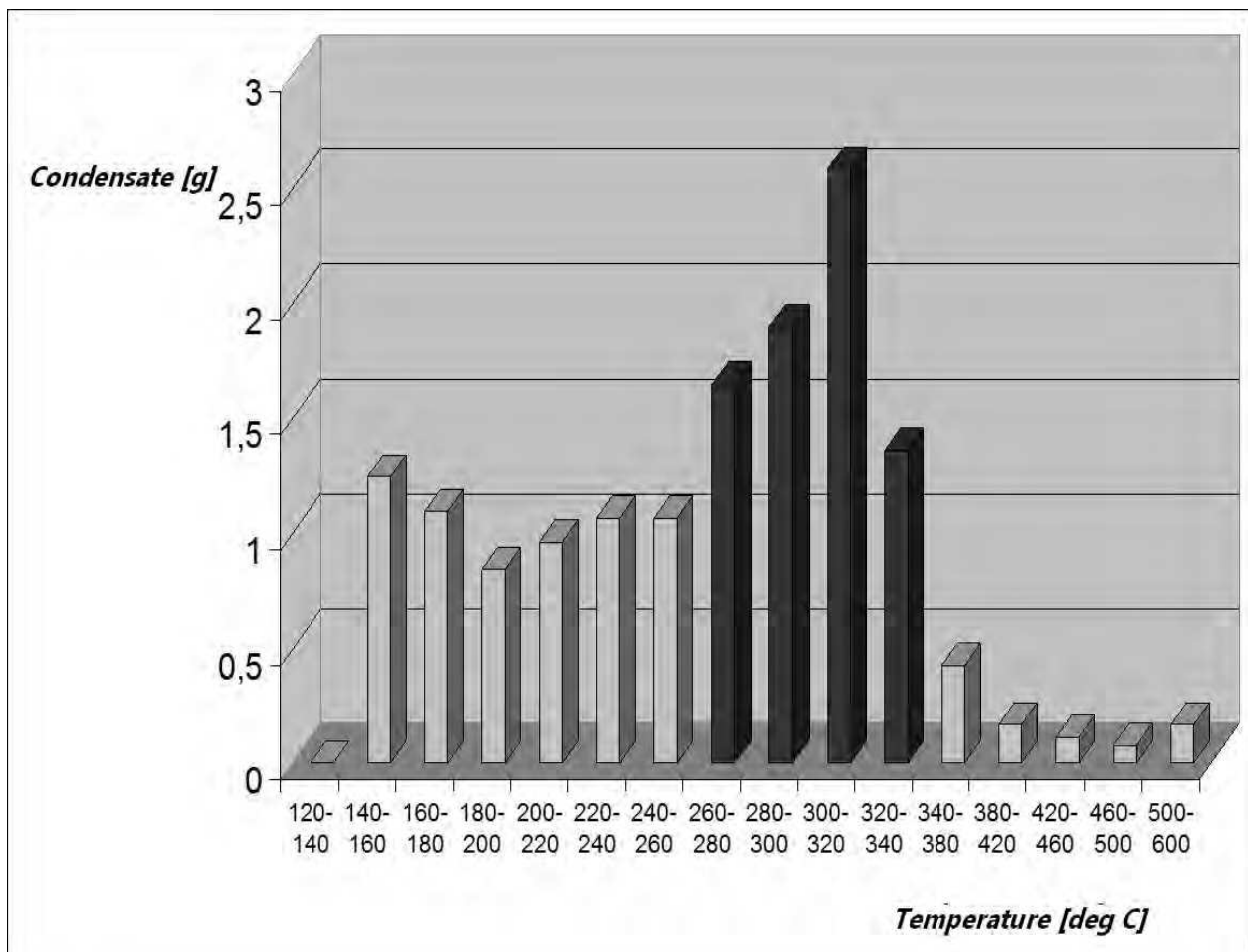


Fig. 16. The intensity of liquid condensate yield (biooil) at different temperatures.

The such collected fraction was considered as a raw biooil subsequently subjected to separation (extraction, chromatography) procedures and chemical characterization. Several instrumental methods were applied: gas chromatography GC-MS (Autosystem XL - MS Turbomass), nuclear magnetic resonance ^1H and ^{13}C NMR (700 MHz Bruker Avance) and infrared spectroscopy FT-IR (Perkin Elmer Spectrum 2000). Additionally the isolated fractions were tested as antioxidants according to ASTM 4871 standard (www.astm.org/Standards/D5770.htm, 2011). The latter procedure consists in the oxidation of a standard substance DBS (dibutyl sebacate) in liquid phase at relatively severe conditions (150 °C, constant flow of air 100 cm³/min). The oxidation may proceed in the presence (1000 ppm) of different protective antioxidants including separated fractions of raw biooil of *Salix viminalis* origin (dry distillation) and some commercially distributed antioxidants like BHT (2,6-di-tert-butyl-p-cresol, buthyl hydroxy toluene, butylated hydroxy toluene). BHT is widely used for the protection and stabilization of cosmetics and food products. The most promising results were achieved so far for two extracts called A and B (ethyl ether and dichloromethane extracts respectively).

The results of a complex analysis (GC-MS, NMR, FTIR, UV-VIS) of both extracts confirm that:

- each extract contains ca. 50 different compounds which may exhibit antioxidative properties,

- most of the potential antioxidants are in fact derivatives of three organic structures (cumaryl alcohol, coniferyl alcohol, synapine alcohol) which are claimed to be units of the biopolymer occurring in *Salix viminalis* wood i. e. lignin (see text above); the compounds are released from the wood sample due to thermolysis of the biopolymer - lignin,
- the extract B contains more furan derivatives while the extract A contains more oxygen heterocyclic compounds.

The determination of the composition of the two preliminary extracts A and B has a certain chemical value but more important is to confirm if the extract theoretically consisting of antioxidant species can exhibit efficient antioxidant activity, what is the main motivation for this research. The absence of such activity could question the whole research attempt which from early beginning was focused on a practical aspects i. e. on the applicability of all products of the dry *Salix viminalis* wood pyrolysis. The preliminary hypothesis was confirmed by the performed controlled oxidation tests (fig. 17). It is visible that the addition of 1000 ppm of a commercial antioxidant i. e. BHT protects the test substance DBS for ca. 50 hours. After this time one observes increasing concentration of some oxidation products in the reaction chamber. In the same experimental conditions pure DBS undergoes instant oxidation without any significant protection time. The addition of the biooil extract B in the same proportion of 1000 ppm extends threefold the protection time. Thus, DBS was protected nearly for one week despite severe experimental conditions. It has to be stated that the protection times for much lower temperatures like room temperature must be very long.

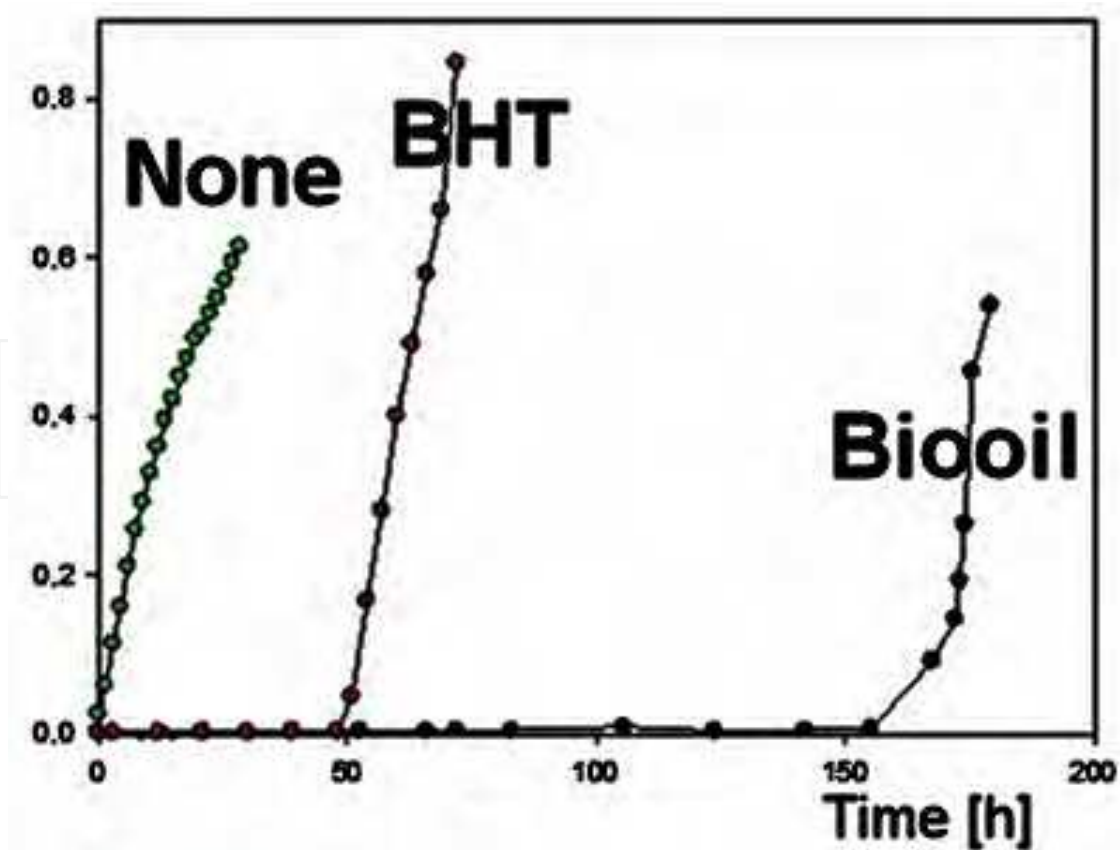


Fig. 17. Restraining of DBS oxidation by means of extract B and BHT.

4. Summary

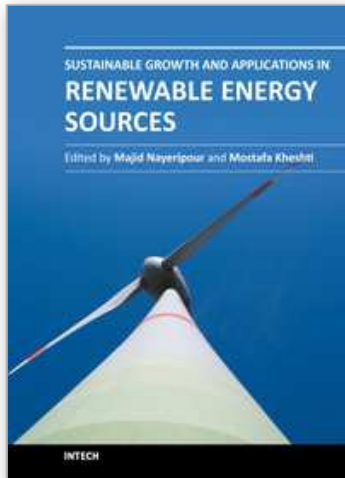
The performer research program prove that *Salix viminalis* is a precious raw material for chemical treatment and it could not be seen only as a fuel for energetic utilization. Its practical value increases regarding that it is easily accessible as agriculture product. It grows fast with a good yield. *Salix viminalis* cultivation has a positive influence on the environment since their high mass productivity per hectare is definitely associated with CO₂ absorption from the atmosphere. The proposed elaboration method is nearly complete since all major products of the wood thermolysis i. e. solid (active carbon of CMS properties) and liquid (biooil containing antioxidants) may find a wide application in practice.

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Worldwide attention to environmental issues combined with the energy crisis force us to reduce greenhouse emissions and increase the usage of renewable energy sources as a solution to providing an efficient environment. This book addresses the current issues of sustainable growth and applications in renewable energy sources. The fifteen chapters of the book have been divided into two sections to organize the information accessible to readers. The book provides a variety of material, for instance on policies aiming at the promotion of sustainable development and implementation aspects of RES.

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