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Properties and Possible Utilization of Waste Generated in the Production of Fibrous Pulp and Paper

Abstract
A considerable amount of waste biomass is generated in the pulp and paper industry which, in the case of landfilling poses a serious burden to the environment. The waste can be utilized as raw material in the production of various products and fuels including combustion with recovery of energy. The physical and chemical properties of various streams of biomass waste in the production of fibrous pulp and paper were examined. It was documented that most of the dry waste display quality parameters close to those of lignite or even coal. A high content of water, which is to be removed to attain a high calorific value, is a drawback of the unprocessed waste. This disadvantage can be excluded by elaboration of energy recovery systems as an alternative to traditional incineration. Such systems used in the utilization of other waste streams are presently being adapted to the waste of the pulp and paper industry. Apart from the physical-chemical identification of the waste, a review was made of commercialized and potential methods to recover energy or substance.

Key words: *waste biomass, pulp & paper industry, utilization.*

Introduction

The generation of waste is inherent in the production of pulp and paper. A variety of substances in the form of water suspension are removed in the course of the production processes from the mass streams and waste water. These comprise waste generated in the production of virgin pulp (debarking, wood-chipping, digestion and pulp purification) and recycled fibre pulp (dissolving, separation of impurities), in the purification of circulating water (clarification) and mechanical-biological treatment of effluents. Waste separated in the manufacture of pulp and paper is a rich source of organic substance that, when recovered, may bring profits both economic and ecological [1]. Results are attainable provided that the hitherto common dumping is abandoned. The recovered raw material or energy carrier would be utilized by harnessing conventional or advanced techniques.

Some of the biomass waste streams from the production of fibrous pulps and paper are today utilized as a source of energy in coal-fired boilers along with solid fuels (e.g. some sediments) or separate incineration in biomass boilers (e.g. bark). In advanced technologies, a more effective use of the biomass potential is sought [1 - 4] like gasification of biomass, generation of syngas, methanol or dimehylether. The purified syngas may be used in the synthesis of a variety of chemical compounds.

The pulp and paper industry generates streams of wastes most of which count as biomass since its organic components are of plant origin. Three different kinds of biomass waste can be distinguished in the production of pulp and paper:

- bark and waste wood (disqualified chips),
- fibrous - so called waste fibre,
- sediments and sludges derived from the waste water treatment.

They are diversified in terms of chemical composition and physical properties depending upon where they were generated [5 - 8]. The characteristic of the waste depends upon:

- kind of pulp and applied technology,
- kind of paper produced,
- kind of raw materials used,
- back-up facilities (equipment, output) both in the production sector and waste management.

The waste is a real burden in the manufacture of paper where it is discharged by dumping in depots. Such management is heavily criticised nowadays for wasting materials and energy, as well as for environmental reasons.

The possible utilization of biomass waste

Ways to recover substance or energy from waste with a high content of organic matter in dry mass that could be of interest to producers of pulp and paper include:

Thermal processes

Incineration with heat recovery

Heat recovery from waste by a direct incineration (generation of steam and electricity) is commonly used in relation to some waste streams like bark and waste wood particularly in pulp mills with installed special bark-fuelled boilers [3, 5, 6]. The method is recommended for other waste streams as well [5, 6] where, however, difficulties are encountered. Whenever coal-fired boilers are in operation, the biomass waste might be burnt along with the coal.

Pyrolysis

In the pyrolysis process [4, 7, 9] (destructive distillation), the organic waste is heated up without the access of oxygen. The process produces a mixture of gaseous and liquid fuels; it is an alternative method to the direct incineration of paper waste and was designed for materials with a high content of carbon, such as waste of wood, crude oil, plastic and rubber. It has yet not been accommodated to the processing of paper waste. Extensive work is being conducted to adopt the method in the utilization of sediments of paper manufacturing [8, 9].

Steam reforming

Steam reforming is based on the innovative technology of impulse incineration which proceeds in a steam reforming reactor. The method used in the utilization of effluent sediments is, however, seen as a technology looming in the processing of paper sludge [8, 10].

Gasification
The method [4, 8, 11], known for many years, has, however, not yet been applied in the utilization of waste from the paper industry. It is viewed as a promising way towards the processing of dewatered paper waste [8, 11].

Chemical processes

Dehydration and hydrogenation
A number of chemical compounds-hydrocarbons can be prepared, first by dehydration of the C_6 and C_5 sugars contained in the lignocellulose biomass to levulin acid and fururol and, then, by thermal de-oxidation and hydrogenation [2, 4].

Hydrolysis and fermentation
The hydrolysis of the lignocellulose biomass to monosaccharides and acetic acid followed by fermentation produces a number of chemicals like ethanol, butanol, acetic acid, lactic acid, and succinic acid [2, 4].

Wet oxidation
Wet oxidation [8, 12] is a process in which organic impurities, both liquid and solid, contained in a liquid are subjected to the action of an oxidant in conditions enhancing their decomposition. The gas delivered in the process holds traces of nitrogen-and sulphur oxides, and suspended dust. Depending on the composition of the purified waste, the delivered gas may also contain volatile organic compounds like aldehydes, ketones and alcohols that can be removed by thermal oxidation.

The technology of wet oxidation has already found application in Europe as a new way of processing paper sludge [8].

Supercritical water oxidation (SCWO)
SCWO is an innovative and effective method of decomposing organic substance contained in effluents and water-containing sediments. The specific properties of water at supercritical conditions are exploited in the method which could be harnessed for the purification of water-containing sediments [8].

Anaerobic fermentation

The biogas-yielding anaerobic fermentation process [8, 13, 14] is primarily applied in animal breeding and in the purification of surplus activated sludge in biological sewage treatment plants. It also finds use in the utilization of solid waste such as communal, agricultural and industrial waste. Industrial waste including paper is usually added to the fermentation of agriculture waste.

Other methods of utilizing the waste, mainly sediments, are seen rather as niches. The following are worth mentioning:

Production of bedding for pets (gravel)
Dried effluent sediments can be used as bedding for pets, e.g. cats. This form of utilization does not look promising considering the amounts and costs [8].

Production of sorption materials
Dried effluent sediments could be used as sorption material to combat leakages of crude-oil products. There are, however, limitations in the amount and price, as above [8].

Carrier of pesticides and fertilizers (active substance)
Dried sediments have the capacity for absorbing active substances. Distributed in plantations, the sediment decomposes delivering the active substance. The decomposition limits the concentration of the active substance in the soil and water and prolongs the action time by a slow release and step-wise fertilization. Delivery of some impurities contained in the sludge and their accumulation in the soil is a drawback of the solution [8].

Conversion to fuel constituents
Levulin acid contained in the sludge can be converted to methyltetrafuran, a compound desired in alternative fuels based on ethanol and natural liquid gas. It improves combustion and reduces emission [8].

Bioconversion to ethanol of the sludge cellulose fraction
The cellulose fraction undergoes an enzyme-catalysed hydrolysis to glucose which is then converted to ethanol by fermentation. The sediment is not always suited to bioconversion as in, for example, the sludge from deinking, because of low cellulose fibre content resulting from the high efficiency of the deinking [8].

Aim and extent of the research

The aim of the investigation was to document the suitability of biomass waste generated in the pulp and paper industry to recover the contained energy through incineration including co-burning with other fuels. It is, for the purpose, important to know the origin and properties of the waste for classification as biomass. Protection of the environment is an important issue in assessing the suitability for the recovery of the waste. The present environment protection regulations do not form a positive basis for the utilization of paper waste, e.g. by the recovery of energy. Consequently, there was no inspiration for systematic investigations into the management of waste generated particularly in the paper industry. Neither provided the reference document of the European Commission PP BREF [5] any detailed information concerning characterization of the waste from the production of pulps and paper and ways of their commercial utilization. Initiating the research in that area, it was recognized that characterization of the paper biomass waste is indispensable for formulating new solutions and procedures which would permit abandoning dumping the waste in the not too distant future.

To realize the adopted aim, examinations were made of the physical-chemical properties of the various streams of biomass waste in the pulp and paper industry. The investigations covered:
- content of dry mass/water
- content of organic matter
- content of mineral substance (ash)
- basic composition of elements: C, H, O, N, S
- total content of chlorine
- heat of combustion
- calorific value
- content of alkaline metals
- content of heavy metals.

Familiarity with and assessment of the physical-chemical properties of the waste streams is a basis for proposing methods of utilization.

Research methods

Investigated materials

Plant-originated waste generated in the production of pulp, recycled fibre pulp, and in the effluent treatment processes were examined, notably:
- Bark from pulp production. The bark is separated in debarking drums in a dry or wet operation.
- Waste wood generated in the preparation of wood for the digestion – wood chipping, chips separation. Content: chips, sawdust, splinters, sawmill type waste.
- Fibrous wastes (rejects) from mechanical fibre separation. Surplus circula-

tion water from paper mill is clarified in a mechanical separation processes. The separated waste mainly contains degraded fibres unsuitable for a secondary use in papermaking, and some amount of paper fillers. Waste from four paper mills was examined.

- Waste material (sludges) from mechanical-biological treatment of paper mill effluents. The waste contains a mixture of dewatered, mechanically separated suspensions (cellulose fibres and mineral fillers) and surplus of activated sludge from biological waste water treatment. Such waste material derived from three integrated pulp and paper mills was examined.
- Waste from deinking of paper for recycling. Paper pulp is derived from recycled paper after its defibration, purification (deinking) and screening. The waste from the purification and screening is composed of a suspension of cellulose fibres and their fine fraction (so called crill), mineral fillers and pigments. The waste is obtained by flotation and dewatering.
- Waste from the preparation of pulp from recovered paper: screening, purification and separation of suspensions. Composition: easy to settle suspensions like cellulose fibre and mineral impurities eg. fillers. The waste is produced in the separation of suspensions and their concentration and dewatering.
- Surplus sludge from biological treatment of paper effluents. Composition: suspension of activated sludge, cellulose fibres, mineral fillers and pigments. Technology of separating the suspension: sedimentation and/or flotation of the suspension along with concentration and dewatering.

Investigation methods

Waste samples were drawn at four Poland-based pulp and paper production facilities. Some lots of the material were collected intermittently from the waste streams of which cumulative batches were made. Samples for testing were drawn from the homogenized cumulative batches. The samples were ground and their physical-chemical parameters were determined in accordance with the below mentioned methods. Appropriate parameters of hard coal and lignite from Polish mines were adopted as reference [15 - 17].

- Total content of moisture: by gravimetric method according to CEN/TS 15414-2:2006.
- Content of dry mass: calculated from total moisture content.
- Content of mineral substance (ash): gravimetric method according to CEN/TS 15403:2006.
- Content of organic substance: calculated from ash content.
- Content of basic elements C, H, O, N: determined using IR automatic analyzer according to CEN/TS 15407:2006.
- Total sulphur content: determined using IR automatic analyzer according to CEN/TS15408:2006.
- Total chlorine content: by microcoulometric method after incineration of the sample in oxygen according to CEN/TS 15408:2006.
- Heat of combustion: calorimetric method according to PN-EN 15400:2011.
- Calorific value: calculated from heat of combustion.
- Content of alkaline metals Na and K: by method of atomic emission spectroscopy (AES).
- Content of heavy metals: by instrumental method ICP OES.

Results

The analysis results are presented in graphs in ***Figures 1 - 7*** and in ***Table 1***. Also shown is the reference value of hard coal and lignite. Following denotation is applied:

Biomass: K – bark, DO – waste wood, ML – fibrous wastes (rejects) from mechanical fibre separation, OMB – wastes from mechanical-biological treatment of paper effluents, OOM – waste from deinking of recycled paper, OM – wastes from the preparation of paper pulp from recovered paper, OB – surplus sludge from the biological treatment of paper effluents. **Fuels**: WK – hard coal, WB - lignite.

All categories of paper waste show high moisture content from 43.2% in the fibrous material from mechanical fibre separation to 79.1% in the biological sludge (***Figure 1***) compared to the reference of hard coal where it is 9.5% in average (from 1 to 18%). Some of the waste had lower moisture content than that of lignite (up to 55%): waste of the preparation of recovered paper pulp – 31.1%, bark – 44%, fibrous wastes from mechanical fibre separation – 43.2%. Consequently, the content of dry mass in these materials was higher than in lignite. Water content was very high in the surplus of activated sludge (79.1%), mechanical-biological sludge (63.4%), waste wood (56.5%) and sludge of the recycled paper deinking (52.5%). The moisture content is presented ***Figure 1***.

The dried paper wastes are characterized by a high content of organic substance (see ***Figure 2***). The sludges from deinking and mechanical-biological treatment show the lowest values of 52.5% and 55.3%, respectively. The content was high in the waste from the preparation of pulp from recovered paper (73.2%), waste wood (98.2%), surplus of activated biological sludge (95.2%), bark (94.9%)

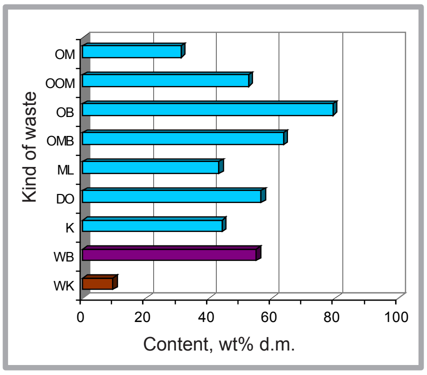

Figure 1. *Moisture content.*

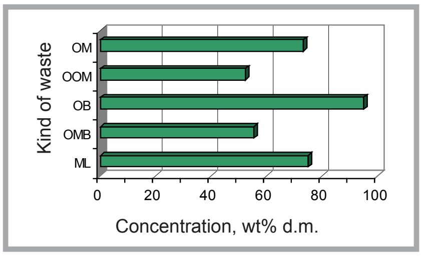

Figure 2. *Content of organic substance.*

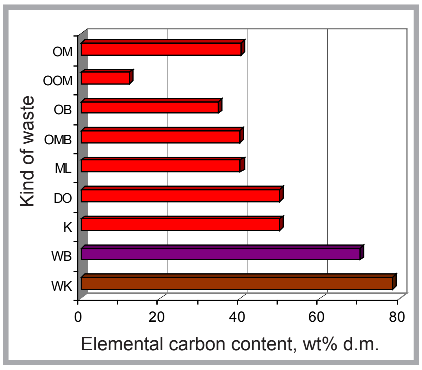

Figure 3. *Average content of elemental carbon.*

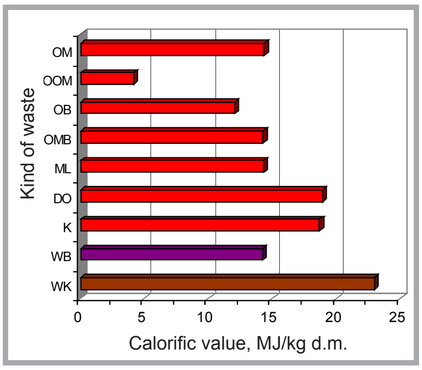

Figure 4. *Average calorific value of the waste, coal and lignite.*

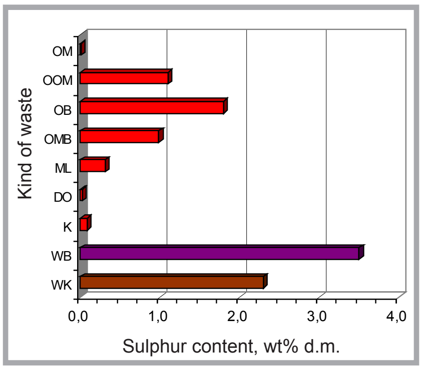

Figure 5. *Average content of sulphur.*

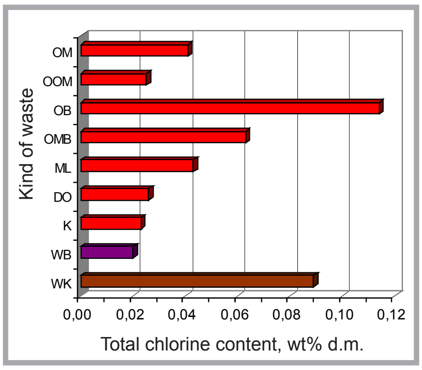

Figure 6. *Average content of total chlorine.*

and fibre rejects from mechanical separation (75.1%).

Content of carbon and hydrogen and the calorific value are important factors when using as a source of energy is concerned. The content of elemental carbon is shown in ***Figure 3*** (see page 175) and the calorific value in ***Figure 4***. The highest content of carbon appears in bark (49.8%) and waste wood (49.7%) The figures were lower in waste of the preparation of pulp from recovered paper (40.2%), fibre rejects from mechanical separation (40.0%), sludges from mechanical-biological treatment (39.9%) and biological sludge 34.4%. The lowest carbon content was measured in the waste of recovered paper deinking – 12.1%. In fossil fuels the carbon content is obviously higher – about 78% in hard coal and 70% in lignite. It is worth mentioning that hydrogen in the biomass waste is an important energy component which, when burnt, does not emit greenhouse gases.

The calorific value of dry biomass waste, coal and lignite is shown in ***Figure 4***. For hard coal the average value is 23.0 MJ/kg (16.7 ÷ 29.3 MJ/kg and for lignite 14.3 MJ/kg (7.5 ÷ 21.0 MJ/kg). The values measured in all of the tested kinds of waste were at a lower level than in coal, however, close to lignite (except one – wastes of the deinking): waste wood – 18.9 MJ/kg, bark – 18.7 MJ/kg which is a little higher than the lowest limit in coal and lignite. In the remaining waste, the values were much lower: fibrous wastes (rejects) from mechanical separation – 14.3 MJ/kg, mechanical-biological sludge – 14.3 MJ/kg, waste from the preparation of recovered paper pulp – 14.4 MJ/kg, surplus activated biological sludge – 12.1 MJ/kg, waste from the deinking of recovered paper – 4.2 MJ/kg.

In regard to environment protection the content of carbon, sulphur and chlorine in the fuels is an important factor. Hazardous gases CO_2, SO_2, HCl and chloroorganic compounds are generated and emitted to the atmosphere. All kinds of the waste tested have shown a lower content of elemental carbon than in the fossil fuels (***Figure 4***) and a low level of elemental sulphur content (***Figure 5***). In all examined waste, the content of sulphur was lower than the average value in lignite (about 3.5%) and hard coal (about 2.3%). It amounted to 1.1% in the deinking waste, 0.3% in the fibrous wastes (rejects) from mechanical fibre separation and was below 0.1% in the remaining ones (bark – 0.08%, waste wood – 0.02%, and 0.01% waste of recycled paper pulp preparation).

Figure 6 shows the average values of chlorine content. The content of the element is low in all examined materials; except the surplus activated sludge. The level of chlorine content is lower than the average content in hard coal 0.089% (0.02 - 0.159%); however, higher than the average in lignite 0.02% (<0.005 - 0.029%). The following are the values for the tested materials: surplus activated sludge – 0.114%, sludge from mechanical-biological treatment – 0.063%, fibrous wastes (rejects) from mechanical separation– 0.043%, preparation of recovered paper pulp – 0.041%, waste wood – 0.026%, waste of deinking – 0.025%, and bark – 0.023%.

All of the tested materials and the reference coal and lignite contained traces of heavy metals; their content is shown in ***Figures 7.a – 7.l*** and in ***Table 1***. In ***Table 1*** values of concentrations of the trace elements which in material of biomass are higher than in reference fuel – (hard coal) were indicated in dark grey. Content of heavy metals such as cadmium, cobalt, chromium, copper, nickel, lead and antimony in the waste

Table 1. *Content of trace elements in the tested biomass materials; ☐ - concentration of the element lower than in hard coal. ■ - concentration of the element higher than in hard coal. ne - not estimated.*

Biomass	Content of trace elements											
	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Sb	Sn	V
Hard coal (WK)	9.00	1.00	9.00	14.0	23.0	0.30	58.0	23.0	27.0	1.00	4.00	39.0
Lignite (WB)	0.80	0.20	1.00	3.60	3.00	0.20	77.0	3.00	3.00	0.80	4.00	10.0
Bark (K)	0.63	0.98	0.40	2.12	1.15	0.02	411	1.15	2.72	0.26	1.14	0.45
Waste wood (DO)	0.17	0.27	0.36	9.44	32.9	0.01	118	33.0	3.10	0.800	0.36	0.74
Paper and fibre sludge (ML)	1.05	1.71	3.62	15.6	6.19	0.33	73.8	6.19	23.3	3.56	3.20	20.2
Waste fom mechanical-biological treatment (OMB)	0.87	3.09	4.47	22.5	11.6	0.17	239	11.6	27.3	4.73	3.65	30.9
Surplus biological activated sludge (OB)	<0.01	0.80	5.18	32.4	16.8	0.33	ne	16.8	21.4	ne	ne	ne
Waste from deinking of scrap paper (OOM)	3.56	0.41	2.57	13.6	14.3	0.03	69.2	14.3	41.7	3.87	4.46	8.53
Waste from pulp screening (OM)	1.37	0.72	5.26	10.3	9.24	0.13	102	9.24	40.0	5.48	1.20	7.67

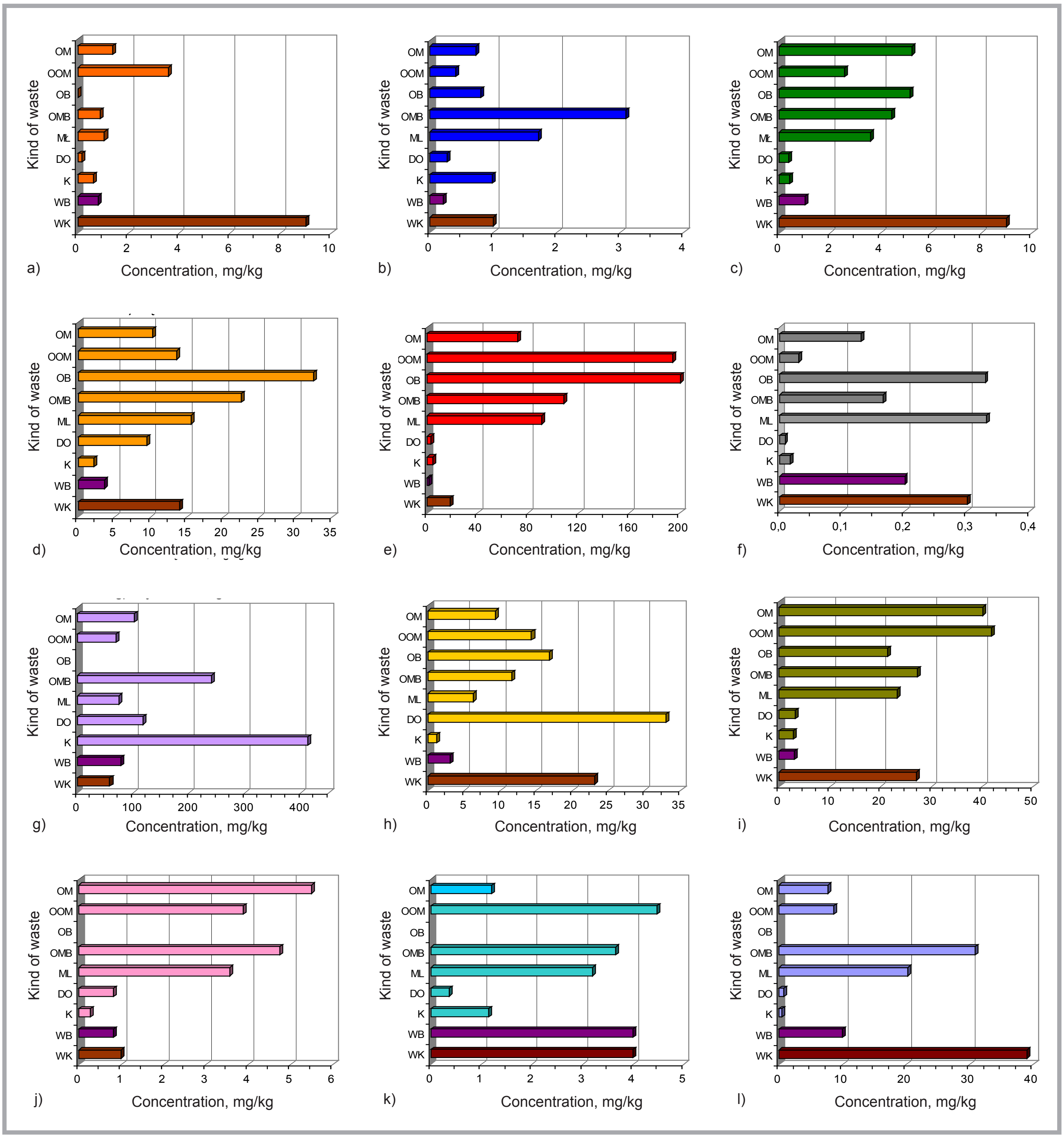

Figure 7. *Average concentration of: a) arsenic, b) cadmium, c) cobalt, d) chromium, e) copper, f) mercury, g) manganese, h) nickel, i) lead, j) antimony, k) tin and l) vanadium in the examined materials.*

of the paper industry was found to be higher than in lignite. The comparison with hard coal looks better (***Table 1***). The reason why the metals appear in the waste is that before the separation into waste, the material particles come in contact with the technology media of the paper mill. Some amounts of the metals like iron, copper, chromium, cadmium, nickel and lead originate from the corrosion of the installation and equipment. Due to the high absorption ability of the cellulosic fibres, particles of the inorganic substance are absorbed on the fibre surface, and a part of the fibre with adhering metals travels to the waste. One other factor increasing the amount of metals is the low fresh water consumption and multiple recirculation of technology water causing an accumulation of the impurities. It should, however, be noticed that the content of heavy metals apart from copper and manganese in the biomass waste remains in the trace range not exceeding 50 mg/kg (0.005 wt%).

Conclusions

1. The investigation and assessment of physical-chemical properties of the biomass waste of the pulp and paper industry confirm the feasibility of utilizing the waste.
2. The wastes generated in the course of pulp and paper manufacture are in the majority of plant origin and may be considered equal with biomass from other sources, equally suited to the production of energy.

3. The investigation confirmed the suitability of the waste from the paper industry for the production of thermal and/or electric energy. The waste after removing water reveals a high calorific value. The wet wastes, for their high content of organic substance, may in the future be used as an energy carrier or raw material in the production of chemicals.
4. In comparison to lignite and hard coal, the examined wastes have a higher content of some of the heavy trace metals, though the content still falls in the trace range (< 0.005%). The higher metal content results from the specific technology in which water is multiply recirculated for the sake of low fresh water consumption.
5. In regard to environment protection, the biomass waste being a renewable source of energy presents itself as a profitable alternative to the incineration of fossil fuel. It is characterized by a lower content of elemental carbon and sulphur which are a source of greenhouse gases – carbon and sulphur oxides.

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