Quality of Life

(Banja Luka)

VOLUME 2 ISSUE 1-2 JUNE 2011 ISSN 1986-602X
The Republic of Srpska, Bosnia and Herzegovina

UDC 616
UDC 637
UDC 613
UDC 541
UDC 316

A Multidisciplinary Journal of Food Science, Environmental Science and Public Health

APEIRON

VOLUME 2
ISSUE 1-2

Quality of Life
(Banja Luka)

A Multidisciplinary Journal of Food Science, Environmental Science and Public Health

PUBLISHED BY PAN-EUROPEAN UNIVERSITY APEIRON BANJA LUKA, BOSNIA AND HERZEGOVINA

Editorial Office
Quality of Life
Pan-European University Apeiron
Pere Krece 13, 78 000 Banja Luka, B&H
Tel: +387 51 247 910
Mob: +387 65 141 619
Fax: +387 51 247 921
e-mail: info@qol-au.com,
sekretar@qol-au.com,
redakcija@qol-au.com
URL: http://www.qol-au.com

Secretary Igor Grujić

Language Editor (English, Serbian)

Technical Editor/Layout Sretko Bojić

Web design Miloš Pašić

Printed by Artprint, Banja Luka
Printed in 300 copies

Aim and Scope

Quality of Life publishes original research papers and reviews and aims to provide a forum for the rapid dissemination of significant novel research in the various disciplines encompassing the Science and technology of food, Public health engineering, Sanitary inspection and control, Environmental and public health. Topics covered by the journal include:

- Dietetics; Nutrition principles applied to foods
- Food Technology; Production and preservation of foodstuffs; Food preservation technique
- Industrial microbiology; Science and technique of applied microbiology; Applied mycology
- Public Health, environment and hygiene
- Hygiene of air, water, soil; Pollution and its control
- Water; Sanitation; Water treatment
- Sewage; Treatment, disposal, utilization of sewage
- Urban hygiene; Wastes; Refuse; Rubbish; Garbage; Collection and disposal of town wastes
- Measures against industrial and other nuisances
- Occupational health hazards; Occupational health and hygiene
- Ecology; Environmental engineering, sustainability and health
- Related topics

UDC 616
UDC 637
UDC 613
UDC 541
UDC 316

Quality of Life is registered with the Ministry of Science and Technology of the Republic of Srpska by serial registration code 07.030-053-160-4/10, date 03.03.2010.
Quality of Life (ISSN 1986-602X) is an international journal published four times a year.

Full-text available free of charge at http://www.qol-au.com

UDC 616
UDC 637
UDC 613
UDC 541
UDC 316

ISSN 1986-602X

Quality of Life

Vol. 2(2011) No.1-2 (1-48)

CONTENTS

Aims, Scope and Editorial Board,

Quality of Life is the first journal we started to publish. Quality of Life specifically focuses on improving life through issues, both within the globe and within regions. It covers broad areas of studies e.g.: Food and Food Engineering, Nutrition and Health, Ecology and Environmental Engineering and related issues of education, science and other, with the purpose to facilitate synergy effects from their interaction and integration that produce value for improving quality of life and social practice.

Quality of Life Magazine is published four times a year: March, July, September and December. The journal can publish: Original scientific papers, Preliminary Communications, Scientific Notes, Reviews and Professional Papers. All works, which will be published in the journal Quality of Life will be reviewed by two reviewers. Language of published papers is English and that is the reason we ask the authors to submit their works in professional English.

Papers that are published in our magazine will be delivered to libraries around the world, and electronic versions of papers published on the web site will be accessible to everyone. Access to electronic database of published papers is free. In other words, authors, and all others who are interested in the published scientific papers can be downloaded for free. In this way, we want to contribute to the free exchange of scientific information between experts in different countries and contribute to the improvement of living conditions of people.

Papers are published in Quality of Life in English, with international serial codes ISSN 1986-602X (Print) and ISSN 1986-602X (Online). Quality of Life is registered with the Ministry of Science and Technology of the Republic of Srpska by serial registration code 07.030-053-160-4/10, date 03.03.2010.

Journal Editorial Board is composed of prominent scientists from eight countries. We invite all interested scientific and professional workers from our country, countries of the region and the world to cooperate, either as authors or as reviewers of papers. In addition, we invite all interested parties to submit their comments, criticisms or opinion, which will help to editorial board and editorial magazines in improving the quality of their work.

Editors

Original scientific paper
UDC: 616.8-056.83:316.624

Isolation of Tomato Seed Oil From Tomato Waste by Application of Supercritical Fluid CO_2 Extraction

Kiril Lisichkov[1], Stefan Kuvendziev
University Ss. Cyril and Methodius, Faculty of Technology and Metallurgy, Skopje, Macedonia
Borce Lisichkov
"VIVA sokovi", Skopje, Macedonia

Abstract: The goal of this work is isolation of tomato seed oil from the tomato waste (skin and seed) from tomato processing industry by utilization of non-conventional, green solvent technology. In the frames of experimental research, the influence of working parameters (temperature, pressure and extraction time) on the total yield of isolated tomato seed oil. Dynamic method for determination of solubility parameter in a supercritical CO_2 has been used to determine the solubility of tomato seed oil in the supercritical CO_2.

Obtained results regarding the influence of operating parameters on total yield of extracted tomato seed oil are presented graphically. The influence of the supercritical fluid' density on the tomato seed oil' solubility was determined based on those results. The chemical composition of isolated tomato seed oil was determined by application of Gas Chromatography.

Keywords: tomato seed oil, solubility, supercritical CO_2

Introduction

Industrial processing of fruits and vegetables results in large accumulation of byproducts that represent potential raw material rich in bioactive components. These tomato processing industry byproducts are sold at low prices or practically given to farmers to be used as cattle food. On the other hand, these byproducts - seeds and skins can be used as a source of vegetable oils and antioxidants (lycopene) by application of appropriate precise process separation methods (Supercritical CO_2 - green solvent) [1].

Non-conventional separation procedure - supercritical fluid CO_2 extraction (SFE-CO_2) conforms to the strict demands of the precise process eco-technologies [2]. It represents a perspective method especially in obtaining eco-friendly extracts from vegetable and animal raw materials. Implementation of SFE for isolation of vegetable oil from tomato seeds results in obtaining high quality and high purity total extract and excludes the presence of organic solvents, heavy metals and some microorganisms [3], [4].

Materials and Methods

Red tomato waste seeds from tomato processing industry were used as a working raw material in the experimental researching. Tomato seeds represent a byproduct of the technological process of processing red tomatoes into tomato concentrate. Tomato waste material had been dried at ambient temperature in absence or direct sunlight. A hydro separation method (G:V = 1:3) was conducted in order to separate tomato seeds from the rest of the waste material, where G - tomato solid waste (skin and seed), V - distillated water. Through the hydro separation process it was established that seeds constitute 37,9 % (wt) of the waste material [5]. After the hydro separation procedure, obtained seeds were submitted to ambient temperature drying process in absence of sunlight. In order to determine the total content of tomato seed oil in tomato seeds, a classical *Soxhlet* extraction process with 70% (vol) ethanol as an extraction solvent, was applied. According to this procedure, the total amount of seed oil is 20.1 % (wt).

Supercritical fluid extraction from working raw material was done in semi industrial pilot plant. The apparatus has extraction and separation vessels of 4 dm^3 and 4 dm^3 in volume, respectively. Maximum working pressure is limited at 500 bar and the extraction temperature can be varied from ambient to 130°C [6]. The sample is loaded into extraction vessel and extracted with supercritical carbon dioxide. Pressure and temperature changes in the separation vessel cause the condensation or precipitation of the soluble components from CO_2 fluid. After separation, CO_2 is recycled.

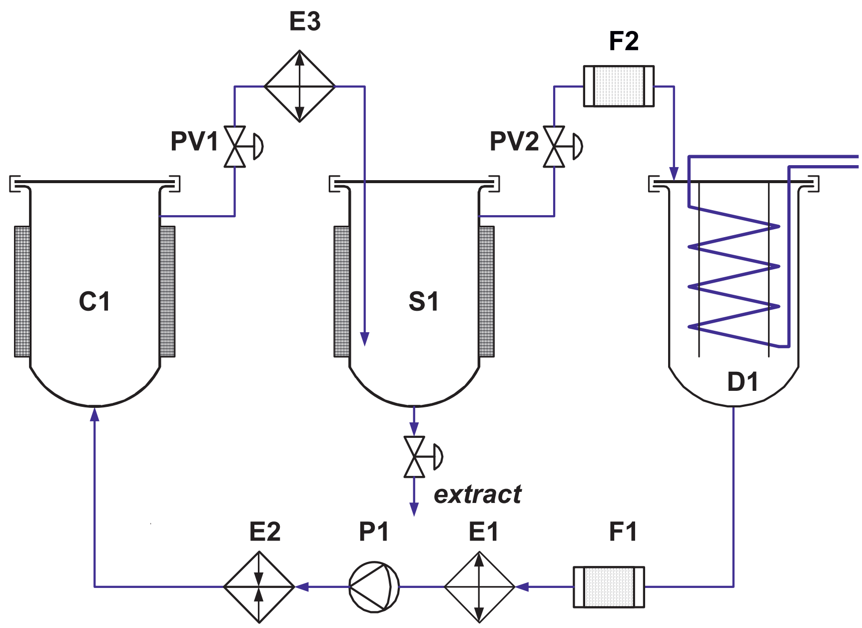


Fig. 1 Schematic flow sheet of supercritical extraction pilot plant (Uhde. Germany)
(C_1 – extractor; S_1 – separator; D_1 – CO_2 tank, $E_{1,2,3}$ - heat exchanger, P_1 - high pressure pump, $PV_{1,2}$ - control valve, $F_{1,2}$ - flow rate control)

Qualitative and quantitative analysis of the obtained extract was performed by GC method. The GC apparatus type was "GL Science GC-353, FID" and silica column type "Chrompack WCOT FFAP-CB, 25 m x 0,32 mm i.d."

Results and Discussion

The influences of working conditions (pressure, temperature and extraction time) on the total yield of extract and its solubility in the supercritical fluid have been examined during the extraction process on tomato seeds. The separation in all of the experiments was conducted at the following operating conditions: operating temperature of 25°C and operating pressure of 50-55 bar.

Obtained results regarding the influence of the operating pressure on the total yield of tomato seed oil are presented graphically:

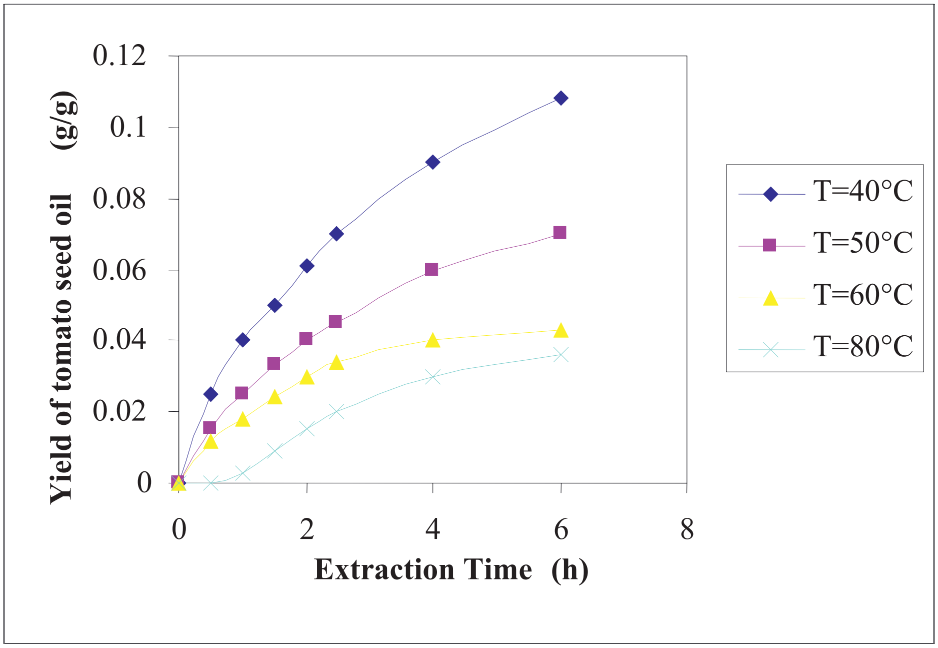


Fig. 2 Influence of operating pressure (P=140 bar) on total yield of seed oil
(Operating conditions: Q= 20 kg CO_2 /h; τ = 6h; W= 7.5%; d= 0.27 mm)

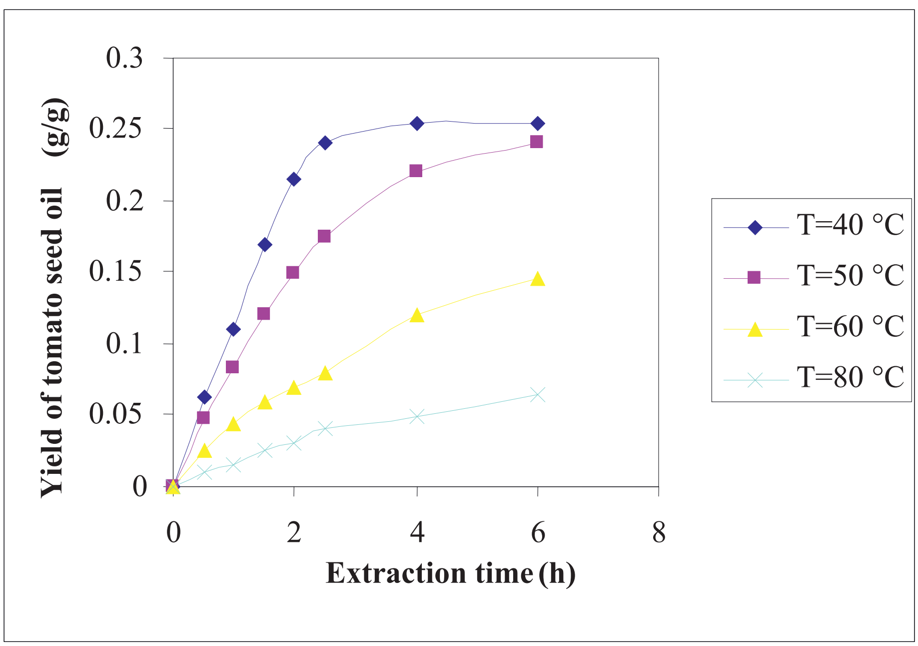


Fig. 3 Influence of operating pressure (P= 210 bar) on total yield of seed oil
(Operating conditions: Q= 20 kg CO_2 /h; τ = 6h; W= 7.5%; d= 0.27 mm)

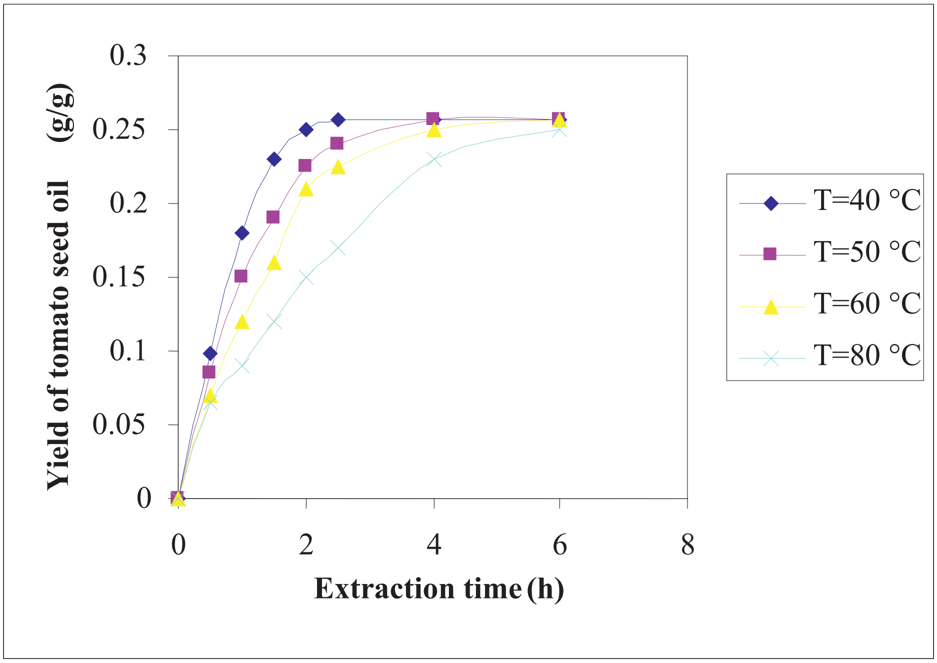


Fig. 4 Influence of operating pressure (P= 280 bar) on total yield of seed oil (Operating conditions: Q= 20 kg CO_2 /h; τ = 6h; W= 7.5%; d= 0.27 mm)

The analysis of above presented results shows that higher operating pressure at operating temperature of 40°C results in increase of the total yield of extract - tomato seed oil. This phenomenon is also characteristic for higher operating temperatures. On the other hand, higher operating temperatures produce lower yield of total extract, which derives from the lower density of supercritical CO_2. Therefore, it can be concluded that the supercritical CO_2 extraction of vegetable oil form tomato seeds is best conducted at lower temperatures and higher operating pressure, in the CO_2 - PT diagram area of highest density of supercritical CO_2. This means that optimal SFE- CO_2 extraction of vegetable oil from tomato seeds can be achieved at operating temperature of 40°C and operating pressure of 210 bar.

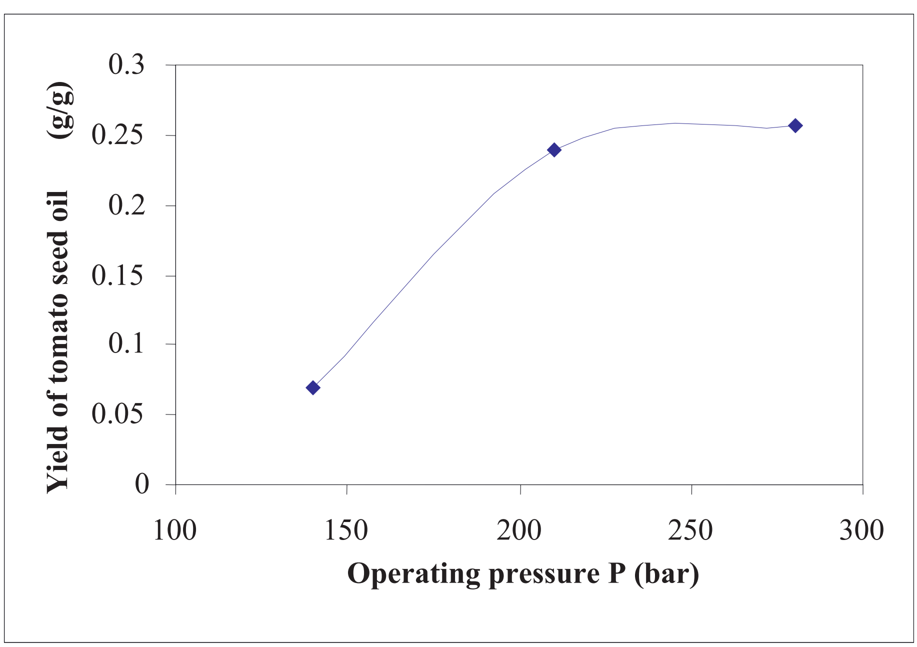


Fig 5. Influence of operating pressure on the yield of tomato seed oil through SFE-CO_2 (Operating conditions: t = 40 ^{0}C; τ = 2.5 h; Q = 20 kg CO_2 /h; d = 0.27 mm; W=7.5 %)

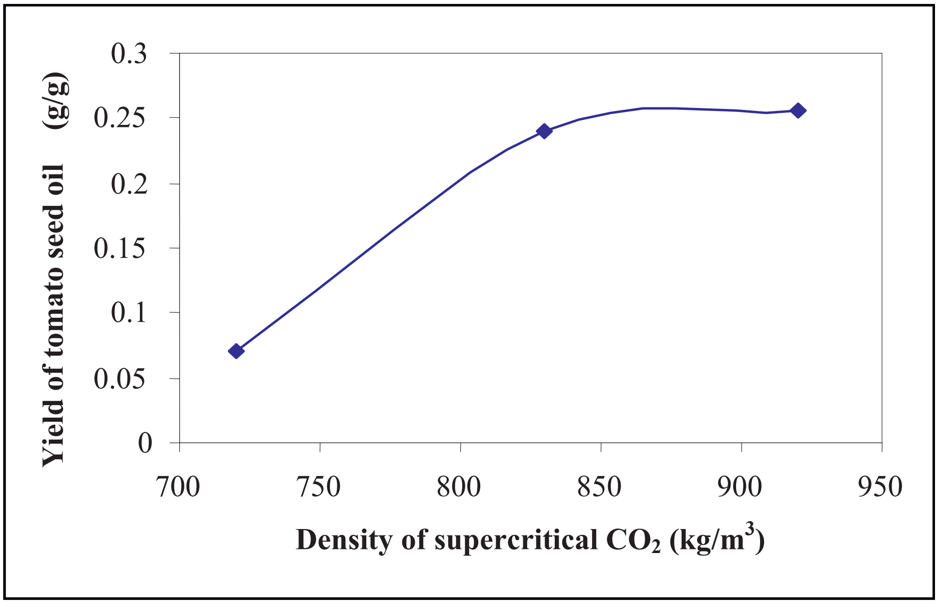


Fig. 6. Tomato seed oil yield variation depending on the density of the supercritical CO_2 at isothermal SFE-CO_2 (Operating conditions: t = 40 ^{0}C; τ = 2.5 h; Q= 20 kg CO_2 /h; d= 0.27 mm; W=7.5 %)

Figures 5 and 6 clearly indicate that an increase of the operating pressure hence increased density of the supercritical fluid, results in higher yield of total extract, when operating at isothermal conditions.

Further experiments (Fig. 7 and 8), conducted in order to determine the influence of the operating temperature, were performed at operating pressure of P= 280 bar. In addition, it has been confirmed once more that an increase of the operating temperature from 40^{0}C to 80^{0}C at isobaric operating regime results in reduction of the total yield of extract. This derives from the poorer solubility of the vegetable oil in the supercritical fluid with lower density.

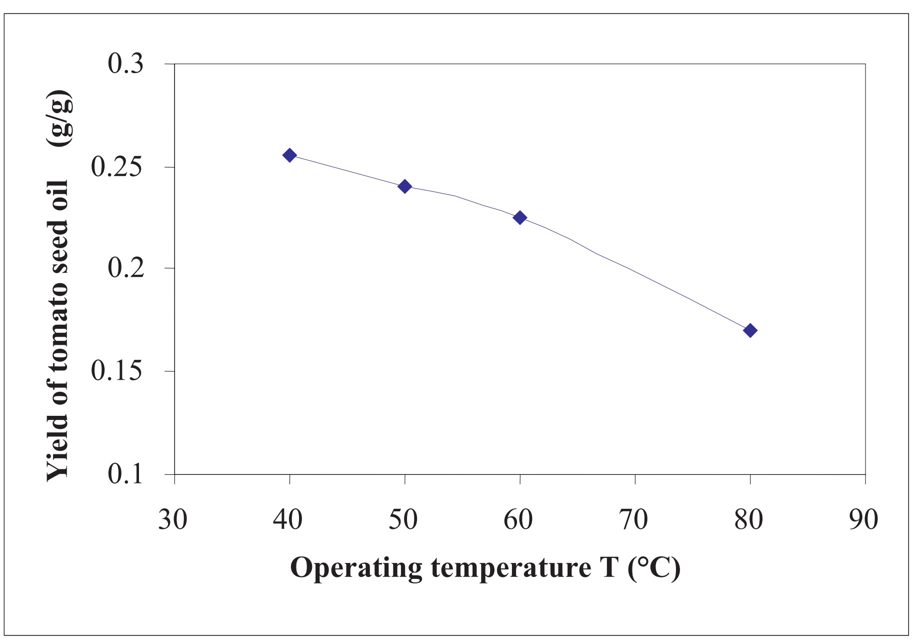


Fig. 7 Influence of operating temperature on tomato seed oil yield at SFE-CO_2 (Operating conditions: P= 280 bar; τ = 2.5 h; Q= 20 kg CO_2 /h; d= 0.27 mm; W= 7.5 %)

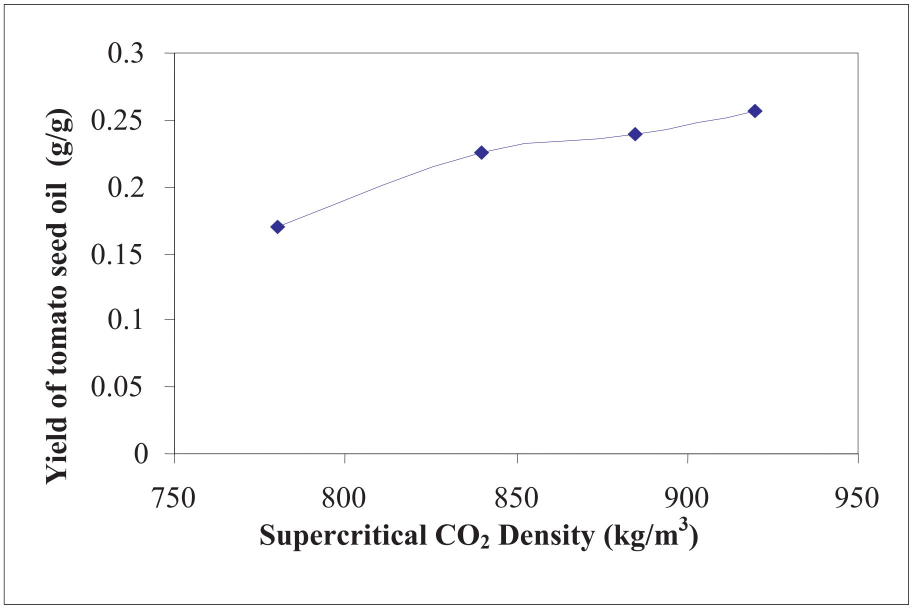


Fig. 8 Tomato seed oil yield variation as a function from supercritical CO_2 density at isobaric SFE-CO_2
(Operating conditions: P=280 bar; τ =2.5 h; Q=20 kg CO_2 /h; d= 0.27 mm; W= 7.5 %)

Series of experiments were performed in order to determine the influence of the extraction time parameter on the yield of vegetable oil, at operating conditions of: P=280 bar and t = 40^0C in a time interval of τ = 0-6 h.

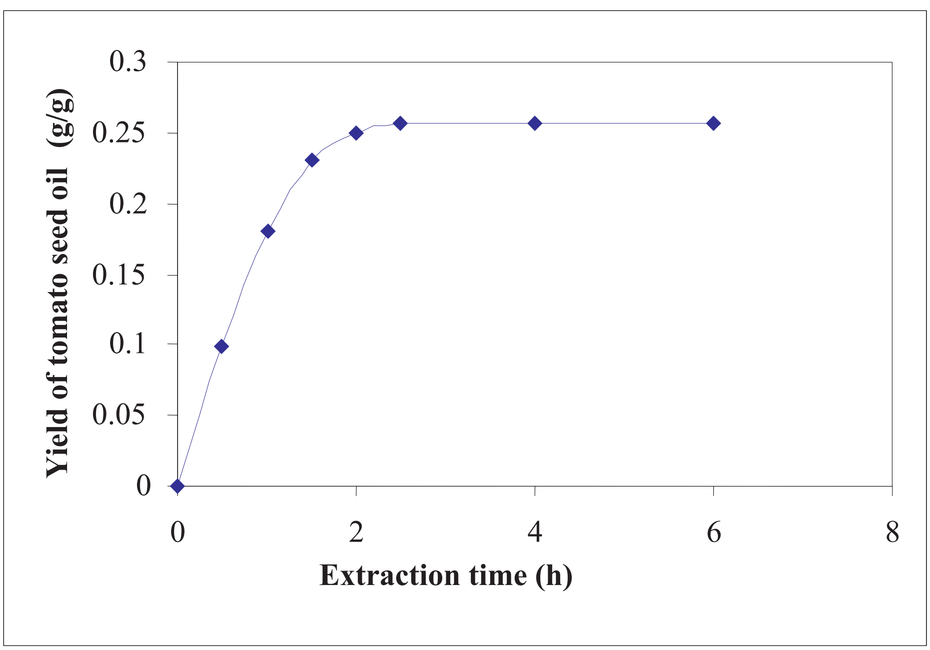


Fig. 9 Tomato seed oil yield variation at SFE-CO_2 as a function of extraction time
(Operating conditions: P= 280 bar; t = 40 ^{0}C; Q= 20 kg CO_2 /h; d= 0.27mm; W= 7.5 %)

Figure 9 suggests that following the initial 2.5 hours, the extraction process enters its equilibrium where a maximal yield of extracted vegetable oil is achieved.

The following figure (Fig.10) presents the functional dependency of tomato seed oil solubility on the operating pressure at various operating temperatures through the SFE-CO_2 process. Obtained results suggest that the highest solubility of tomato seed oil is achieved at operating pressure value of 210 - 280 bar interval and at operating temperature of 40^{0}C.

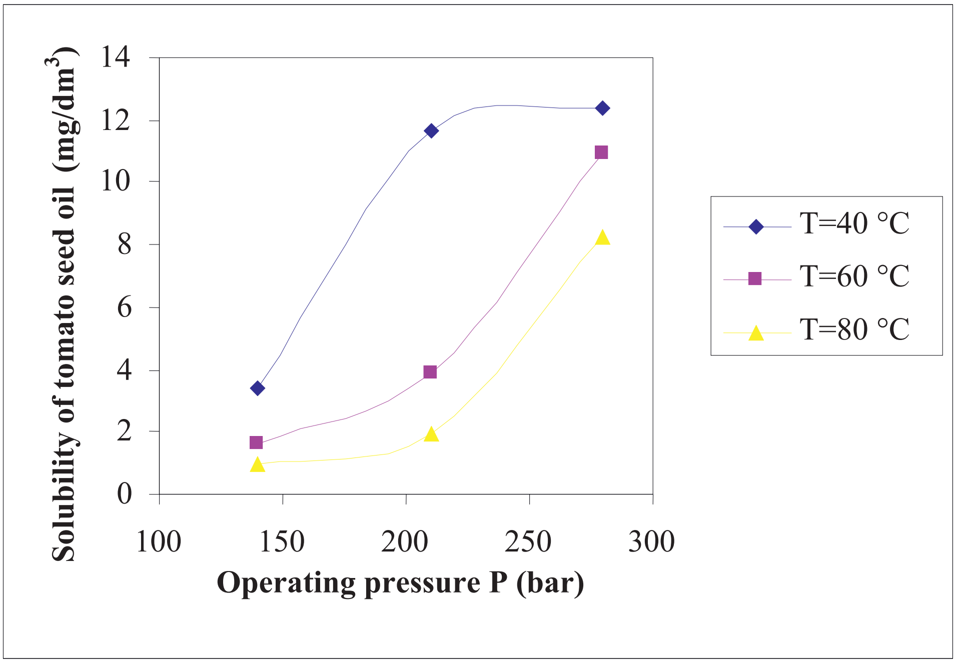


Fig. 10 Tomato seed oil solubility as a function of operating pressure
(Operating conditions: Q= 20 kg CO_2 /h; W= 7.5 %; τ = 2.5 h; d= 0.27mm)

Process parameters' legend:
Q - supercritical CO_2 flow rate [kg/h]
W - raw material humidity [% wt]
d - particle granulation [mm]
τ - extraction time [h]

Quantitative analysis of isolated tomato seed oil by application of Gas Chromatography (GC)

Obtained results regarding the quantitative presence of unsaturated fatty acids through application of gas chromatography on the isolated tomato seed oil are presented in the following table:

Table 1. Unsaturated fatty acid composition (% W/W) in tomato seed oil isolated at P= 280 bar; t = 40^{0}C

Time (min)	Yield (%)	C (16:1)	C (18:0)	C (18:1)	C (18:2)	C (18:3)
5	10.2	1.89	5.54	20.96	53.2	5.6
20	27.5	1.99	5.5	20.58	54.0	6.0
30	38.1	2.1	7.2	23.1	53.8	5.8
60	69.5	1.6	7.4	23.2	53.85	6.32
100	94.5	2.86	9.85	24.7	47.1	5.9
140	99.2	4.2	12.5	26.5	40.3	5.01

According to the obtained results regarding the composition of the tomato seed oil, it is evident that the unsaturated fatty acid - linoleic acid (C18:2, $C_{18}H_{32}O_2$, omega-6) constitutes the highest share of the tomato seed oil composition.

Conclusion

Based on the presented results, following conclusions can be drawn:

- Conforming to the zero emission process concept, tomato waste can be utilized for isolation of high quality tomato seed oil, rich in bioactive components, which are of significant importance to the cosmetic, pharmaceutical and food industry;
- Tomato seed oil, isolated and purified through SFE-CO_2, represents potential raw material for a design of new bioactive products. Considering its physical and chemical properties, tomato seed oil is a potential source of unsaturated essential fatty acids. The quantitative ratio of the unsaturated fatty acids is more suitable to the demands of the cosmetic formulations then the same soya ratio;

Overall, considering all of the obtained results, an appropriate procedure for utilization of tomato waste from the canning industry, can be established in order to obtain useful final products.

References

[1] Reverchon E., De Marco I. (2006), Supercritical fluid extraction and fractionation of natural matter, J. Supercrit. Fluids 38 (2) 146-66.

[2] Reverchon E., Marrone C. (2001), Modeling and simulation of the supercritical CO_2 extraction of vegetable oils, J. Supercrit. Fluids 19 (2) 161-75.

[3] Lisichkov B. (2007), Model development for design and optimization of mass transfer performances with simulation of high pressure extraction, MS thesis, Faculty of Technology and Metallurgy, Skopje, Macedonia.

[4] Santos R., Lu T., Schlieper L., King M.B., Bastos J. (1996), Extraction of useful components from herbs using supercritical CO_2: experimental findings and data modelling. *3rd International Symposium On high-pressure engineering;* von Rohr, Ph. R., Trepp, Ch., Eds.; Elsevier: Amsterdam; p 399.

[5] Beveridge T.H.J., Girard B., Kopp T., Drover J.C.G. (2005), Yield and composition of grape seed oils extracted by supercritical carbon dioxide and petroleum ether: varietal effects, J. Agric. Food Chem. 53 (5) 1799-804.

[6] Del Valle J.M., De la Fuente J.C., Cardarelli D.A. (2005), Contributions to supercritical extraction of vegetable substrates in Latin America, J. Food Eng. 67 (1/2) 35-57.

Recived: 21.02.2011.
Accepted: 20.06.2011.

Original scientific paper UDC: 616.8-056.83:316.624

Production and Characterization of Glass-Ceramics From Waste Materials

Biljana Angjusheva
Faculty of Technology and Metallurgy, University "St Cyril and Methodius"
Rudjer Boskovic 16, Skopje, Republic of Macedonia
E-mail: biljana@tmf.ukim.edu.mk

Abstract: The fly ash, produced by power plant in Republic of Macedonia have been milled and sintered with addition of waste glass to obtain glass-ceramics. The physical, chemical and mechanical properties of fly ash and waste glass were determined. Through adequate sintering time and temperature, the glass-ceramic materials were manufactured. Chemical, physical and mechanical properties of the obtained composites were defined. The optimal composition of the composite was fly ash with the addition of 40% waste glass. Optimal sintering condition was 1000^{o}C with 1h isothermal time at final temperature and heating rate of 10^o/min. The addition of 40%wt of waste glass in the fly ashes increased the E-modulus from 4.24±1 to 30.55±2 GPa and increased the bending strength from 9.93±1 to 63.18±4 MPa Porosity of the compacts decreased from 44.34±3 to 14.32±2%. Investigation of durability of the produced systems did not show presence of any harmful elements in the obtained solution.

Owning to combination of the macroscopic appearance, microstructure, mechanical and thermal properties developed, dense materials could be used in the civil engineering.

Key words: ceramics, glass-ceramics, composites, coal fly ash

Introduction

Disposal of industrial waste in landfill sites is not a proper solution from economic and environmental consideration. This is related to coal fly ash obtained through combustion of coal and trapped within the power plant by an electrostatic precipitator. Fly ash available as a fine powder presents a valuable source of minerals containing SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O and other oxides. A number of methodologies of treatment and recycling have been developed to minimize the harmful effects in the environment caused by the landfill disposal [1-3]. According to [4] the highest utilization of coal fly ahs is in the construction industry either as addition in concrete or supplement in cement. There are several reports for various application of fly ash in ceramic and glass-ceramic materials [5-7]. Rozenstrauha et al. [8] investigates the influence of various addition on a microstructure and mechanical properties of glass-ceramics obtained from silicate waste. The most commonly used procedure for treatment of industrial waste is vitrification [9], [10], but one of the main disadvantages of the process is the high cost involved, since it is an energy intensive process. The aim of this paper is to demonstrate the possibility of obtaining a dense glass-ceramic composite using high percentage of industrial waste and waste glass with reducing the sintering temperature due to the presence of liquid phase. Furthermore, by using waste glass ecologically, hazardous components are fixed at the molecular level in the silicate phase and inserted additionally in the matrix based on waste material.

The principle of this procedure was presented as a multibarier-concept by Ondracek [11] and basically investigated for various waste combinations. The new glass-ceramic composites possess significantly higher mechanical properties and lower leaching behavior. Dense glass-ceramic materials can be used as building materials.

Materials and methods

The raw materials, fly ash, were taken from thermal power station from Republic of Macedonia (REK Bitola), in further text coded FA and laboratory waste glass mark Pyrex coded WG. Chemical analysis of the fly ash was carried out by X-ray Fluoroscence, model ARL 9900XP. Chemical composition of the waste glass was declared from the manufacturer Pyrex [12]. XRD studies of the samples were realized by using a Philips X-ray diffraction unit (Model PV 105-1) operating at CuK_{α} - radiation. Scanning electron microscopy (SEM) investigations were conducted in JSM - 6460LV, JEOL, using standard metallographic techniques for preparation of the specimens followed by coating of the samples with a thin layer of gold in instrument BAL – TEC SCD 005.

The raw materials were ground in the planetary mill (Fritsch pulverisette 5) during 120 min and screened through a 63 μm screen.

Pressing of the samples was performed by uniaxial press (Weber Pressen KIP 100) at P=45 MPa using PVA as a plastificator.

Sintering of the compacted samples was realized in the chamber furnace in the air atmosphere at temperatures 900, 1000, 1050, 1100^{0}C, using heating rate of 10^{0}C/min and isothermal treatment at the final temperature of 60 min. Bulk density of the sintered samples was determined by water displacement method according to EN-993. The value of theoretical density of the compacts was calculated based on the composition of the initial mixture and known densities of the FA and WG.

Measurements of the mechanical properties (E-modulus and bending strength) of the dense specimens were made on three point bending tester (Netzsch 401/3), where a 30 mm span and 0,5 mm/min crosshead speed were used . Sample shrinkage (%) was determined from the differences in green and fired samples length. Porosity of the samples was calculated from the relative density.

Thermal investigations were perform on the dilatometer Netzsch 402E in the air atmosphere and temperature interval RT-650-RT, with heating rate of 5^{0}C/min. Technical coefficient of thermal expansion of the waste glass was declared from the manufacturer Pyrex [12]. Durability of the obtained materials was tested using the standard methods for glass-ceramics materials. The durability was determinated as a mass loss in 0.1mol/dm^3 HCl, 0.1 mol/dm^3 Na_2CO_3 solutions and in distilled water.

Results and discussion

The chemical composition of the investigated waste materials is given in Table 1.

Table 1. Chemical composition of the industrial waste

Oxide	FA [wt%]	WG [wt%]
SiO_2	50.33	83.34
Al_2O_3	18.59	1.33
Fe_2O_3	7.71	/
CaO	13.76	0.03
MgO	3.05	/
Na_2O	1.07	4.08
K_2O	1.41	0.04
SO_3	1.41	/
B_2O_3	/	11.19
Weight loss	2.60	/
Σ	99.96	100

Investigated fly ash consists highly amount of SiO_2, Al_2O_3 and Fe_2O_3, significant levels of MgO and other alkali metal oxides. It also possesses relatively high level of CaO and belongs to a class C which is in accordance with the literature [13]. XRD analyses of the FA is shown in Table 2.

Table 2. XRD analysis of the fly ash

Material	Composition
FA	quartz, anorthite, albite, hematite anhydrite and amorphous phase

Fig. 1 shows morphology of the FA particles and Fig. 2 presents particles of WG. Fig. 1 confirms that the size of the particles has a diameter of the FA ranging from 5 to 100 μm. Larger particles have irregular shape and size, spherical and partially spherical particles are smaller. The particles of WG have irregular geometry and dimensions between 10-60 μm. (Fig. 2)

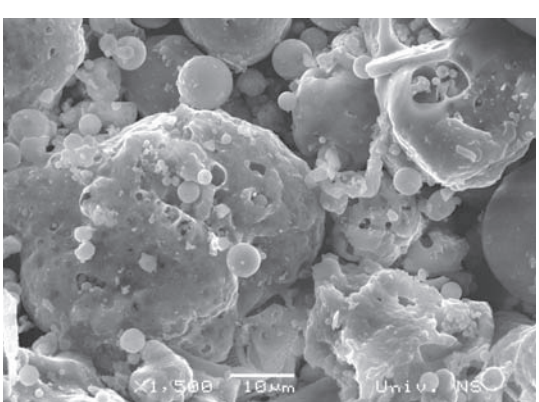


Fig 1. SEM micrograph of the FA, (1.500 χ, bar10 mm)

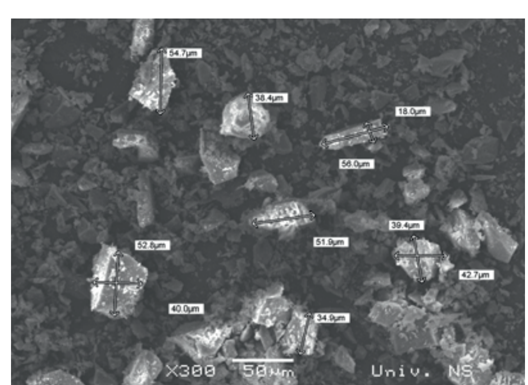


Fig 2. SEM micrograph of the WG, (300χ, bar 50 mm)

Investigations of the sintering studies, for compacts produced from FA point, show that relative density of 90% was achieved at 1100^{0}C and holding time of maximal temperature of 1h. The relative density of 85% was achieved for compacts obtained from WG sintered at 700^{o}C and holding time of maximal temperature of 1h. Density, bending strength, E –modulus, porosity and linear shrinkage of the compacts are shown in Table 3.

Table 3. Sintering temperature, Density, bending strength, E –modulus, porosity, linear shrinkage and technical coefficient of thermal expansion (a_{tech}) of the investigated materials

Compacts	**Sinter.temp./ Time [^{0}C/h]**	ρ **[g/cm^3]**	σ **[MPa]**	E **[GPa]**	Θ **[%]**	ΔL/L **[%]**	α_{tech} **10^{-6}/^{0}C**
FA	900/1h	1.411	6.22	3.29	45.25	1.14	/
FA	1000/1h	1.453	9.93	4.24	44.34	1.80	7.3
FA	1050/1h	1.482	16.50	6.76	42.48	2.96	/
FA	1100/1h	2.340	60.98	30.53	10.01	16.00	/
WG	700/1h	2.233	69.08	27.31	14.43	15.77	3.3

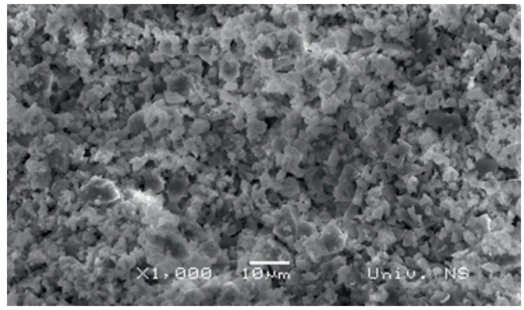
Glass-ceramics composites were obtained by adding the WG in quantity of 10-50% wt. into fly ash. One of the reasons for this was to increase mechanical properties and to decrease sintering temperature, and secondly, to encapsulate the particles of industrial waste into matrix. Dense composites with different densities were obtained by variation of the sintering temperature 900, 1000, 1050^{0}C. Sintering of the compacts FA50WG at 1000^{o}C and higher was not possible because it leads to a degasation and deformation of the compacts. Optimal composition of the composites obtained at optimized sintering temperature, their relative density, E-modulus and bending strength, porosity, and linear shrinkage of composites are shown in Table 4.

Table 4. Sintering temperature, Density, bending strength, E –modulus, porosity, and linear shrinkage of composites

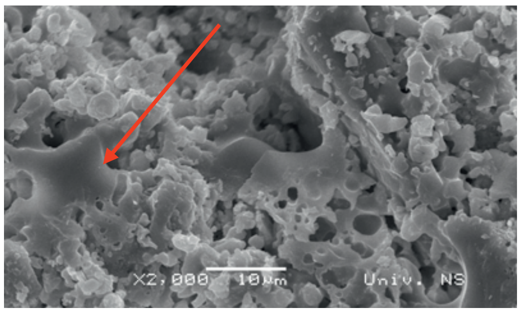
Compacts	**Sinter.temp./Time, [^{0}C/h]**	ρ **[g/cm^3]**	σ **[MPa]**	E **[GPa]**	Θ **[%]**	ΔL/L **[%]**
FA10WG	1000/1	1.568	30.56	10.87	39.94	4.32
FA40WG	1000/1	2.180	63.18	30.55	14.32	15.95

From the Table 3 and Table 4 it is evident that glass addition increases bending strength from 9.93±1 to 30.56±3MPa for FA10WG and 63.18±4 MPa for composite FA40WG, sintered at 1000^{o}C/1h. Increasing of E-modulus is also significant, ranging from 4.24±1 to 10.87±2 and 30.55±3GPa. Porosity of the compacts decreases from 44.34±3 for the compacts of FA to 14.32±2 for compacts FA40WG. Shrinkage of the samples increases from -1.8±0.5 for compacts of FA to -15.95±2 for compacts FA40WG.

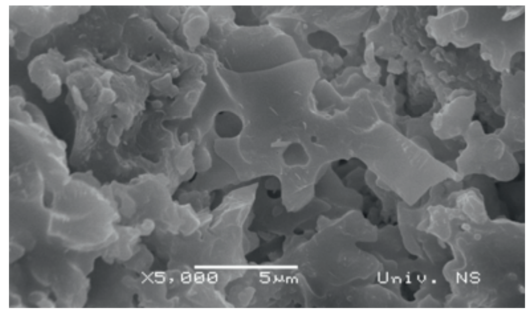
Fig. 3 presents microstructure of the fractured surface of the samples of FA10WG sintered at 1000, and with 1 h of holding at the final temperature and the heating rate of 10^0/min.



(a), bar 10µm



(b), bar 10µm



(c), bar 5µm

Fig. 3 SEM image for FA10WG, t=1000/1h (a-1000χ, b-2000 χ, c-5000 χ,)

Fig. 3 shows that the fractured surface of the sample is rough and granular. On some parts, the presence of the liquid glassy phase [arrow, Fig 3(b)] is evident, but the grains from the original morphology of the FA particles and WG are also recognisable. This confirmed EDS analysis (Fig. 4) on the fractured surface of the samples FA10WG sintered at 1000^{o}C, and heating rate of 10^{0}/min. Spectrum 1 mainly consisting of SiO_2 points to a honey comb particle from diatomei originated from the fly ash. Point 2 corresponding to the composition of the FA and the point3 could be characterized as the region of the glassy phase.

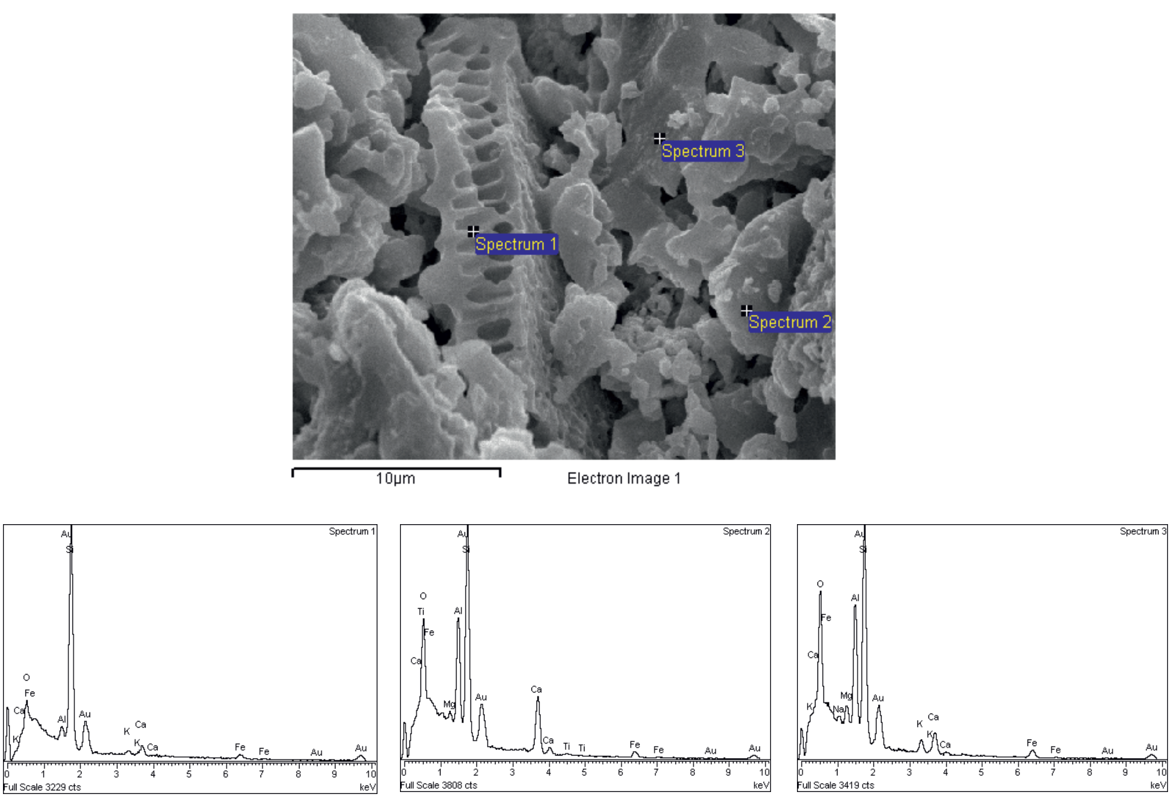
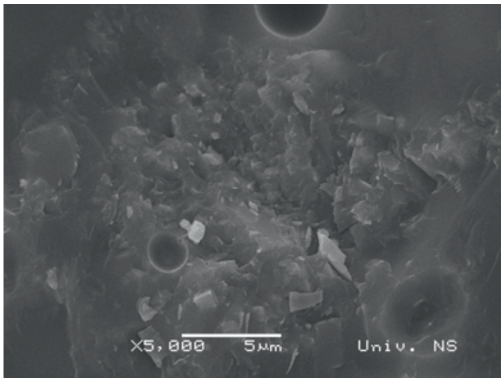
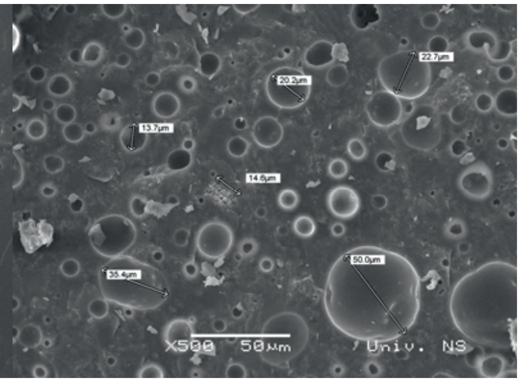
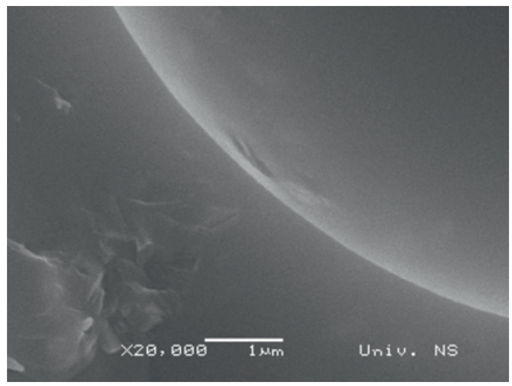


Fig. 4 SEM micrograph and EDS spectrums (1-3) of composites FA10WG, t=1000^{o}C, (bar 10µm)





(a), bar 50 μm (b), bar 5 μm



(c), bar 1 μm

Fig. 5 SEM image for FA40WG, t=1000/1h(a-500 χ, b- 5000 χ, c- 20000 χ,)

Fig 5 shows the microstructure of the composites FA40WG, sintered at 1000^{o}C and at the heating rate of 10^{o}/min.

Fig 5 shows that the microstructure of the fractured surface of the ceramic samples obtained from FA40WG and sintered at 1000 ^{o}C is homogeneous and smoother compared to the FA10WG [Fig 3] sintered at the same temperature. There are no recognisable grains from the FA and they are well incorporated in the silica matrix. There is a significant formation of unconnected spherical pores with dimensions between 5-50μm. According to [13], formation of the spherical pores is connected with softening of the glassy phase and evolution of gas. They pointed that similar pyroplastic effects have been observed in other materials where the gas generation is reported to be due to the decomposition of alkaline metal salts. Fig 6 shows the EDS analysis of the compacts of FA10WG sintered at 1000^{o}C, and at the heating rate of 10^{0}/min. Point 1 is region mainly consisting of silica from the WG. Point 2 could be characterized as the region where FA particles are well embedded in the glassy matrix.

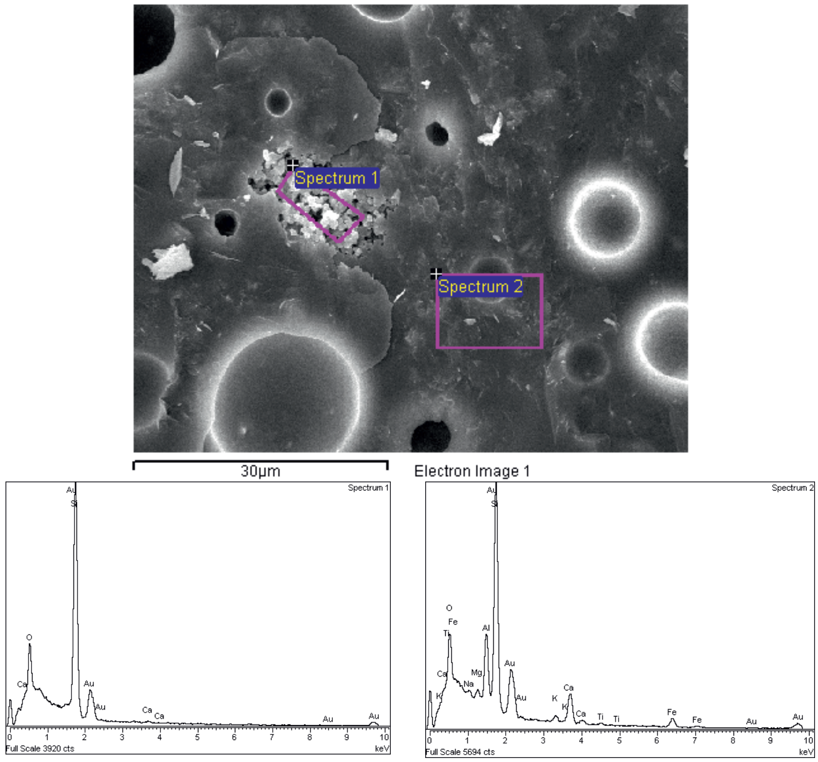


Fig. 6 SEM micrograph and EDS spectrums (1-2) of composites FA40WG, t=1000°C, (bar 30µm)

Temperature variation of the physical coefficient of thermal expansion presented as a second order polynomial form, and values of the technical coefficient of thermal expansion are shown in Table 5.

Table 5. Temperature variation of the physical coefficient of the thermal expansion and technical coefficient of thermal expansion (α_{tech})

Composite	$\vartheta(\Delta L/L_o)/\vartheta T=f(T)$	α_{tech} $10^{-6}/^{0}C$
FA10WG	$-0.0004+6\cdot10^{-5}T-6\cdot10^{-8}T^2$	6.40
FA40WG	$-0.0003+4\cdot10^{-5}T-6\cdot10^{-8}T^2$	5.91

Obtained values for technical coefficient of thermal expansion correspond to the value for technical coefficient reported in the literature [14].

Durability (mass loss after 30 days) of the compacts FA10WG, FA40WG was 4.5% and 2.3% in 0.1M HCl while 0.45% and 0.3% in 0.1M Na_2CO_3 respectively. Atomic absorption spectroscopy did not show presence of any harmful elements in the obtained solution.

Conclusions

- Glass-ceramics materials can be obtained from fly ash and waste glass;
- Optimal sintering condition was 1000°C with 1h isothermal time at final temperature and heating rate of 10°/min;
- The composite produced with addition of 40% wt WG and fly ash shows density of 2.180 g/cm³;

- The addition of 40 %wt WG glass to FA increased the bending strength from 9.93±3 to 63.18±4 MPa and E-modulus from 4.23±2 to 30.55 ±3 GPa;
- Porosity of the composites is 14.32 ±2%;
- Linear shrinkage of the composite specimens is -15.77±2%;
- Dilatometer investigation has shown absence of the hysteresis effect, proving that the systems are in thermal equilibrium;
- Investigation of the durability on the glass-ceramics materials did not show presence of any harmful elements in the obtained solution;
- The chemical and physical properties of the dense materials make them suitable for a wide range of applications in the building industry.

References

[1] J. P. Wu, A.R. Boccaccini, P. D. Lee, M. J. Kershaw, R. D. Rawlings, (2006). Glass ceramic foams from coal ash and waste glass: production and characterization. Advances in Applied Ceramics, 105 (1), 32-9.

[2] J. Bossert, E. Fidancevska, B. Mangutova, B. Panova, D. Milosevki, M. Milosevski, (2004). Liquid phase sintereing of dence and porous glass-ceramics from coal fly ash and waste glass. Sciense of Sintering, 36, 87-92.

[3] R. Giere, L. E. Carleton, G. R. Lumpkin, American Mineralogist, (2003). Micro-and nanochemistry of the fly ash from a coal-fired power plant. 88, 1853-65.

[4] O. E. Manz, (1997). Worldwide production of coal fly ash and utilization in concrete and other products. Fuel, 76(8), 691-6.

[5] C. Leroy, M. C. Ferro, R. C. C. Monteiro, M. H. V. Fernandes. (2001). Production of glass-ceramics from coal ashes. Journal of European Ceramic Society 21,195-202.

[6] J. P. Wu, R. D. Rawlings, A. R. Boccaccini, I. Dlouhy, Z. Chlup. (2006). Waste Not, Want Not-An Inexpensive Glass-Ceramic from Waste. The Glass researcher, 15(2), 29-32.

[7] R. D. Rawlings, J. P. Wu, A. R. Boccaccini. (2006). Glass-ceramics: Their production from waste-Areview, Journal of Mater. Sci. 41, 733-61.

[8] I. Rozenstrauha, D. Bajare, R. Cimdins, L. Berzina, J. Bossert, A. R. Boccaccini. (2006). The influence of various additions on a glass-ceramic matrix composition based on industerial waste. Ceramics International, 32, 115-9.

[9] P. A. Bingham, R. J. Hand. (2006). Vitrification of toxic waste: a brief review. Advances in Applied Ceramics, 105(1), 21-31.

[10] I. A. Soboleb, S. A. Dimitriev, F. A. Lifanov, A. P. Kobelev, S. V. Stefanovsky. (2005). Glass Technol., 46 (1), 28-35.

[11] G. Ondracek. (1994). Waste treatment and recycling to remineralized products with multibarriers structure, Monatshefte, 7, 273.

[12] HYPERLINK "http://www.scilabware.com/Glass_technical/" www.scilabware.com/Glass_technical/, Accessed 15 June 2011.

[13] M. Ilic, C. Cheeseman, C. Sollars, J. Knight. (2003). Minerology and microstructure of sintered lignite coal fly ash. Fuel, 82 (30), 331-6.

[14] M. Erol, U. Demirler, S. Küçükbayrak, A. Ersoy – Meriçboyu, M. L. Öveçoğlu. (2003). Characterization investigation of glass-ceramic developed from Seyitomer thermal power plant fly ashes. Journal of the European Ceramic Society, 23, 757-63.

Recived: 24.02.2011.
Accepted: 20.06.2011.

Original scientific paper UDC: 616.8-056.83:316.624

Biocomposites Based on Poly (Lactic Acid) and Their Recyclability

Vineta Srebrenkoska[1]* and Gordana Bogoeva Gaceva[2]
[1]Faculty of Technology, Goce Delčev University, "Krste Misirkov" Štip, Republic of Macedonia
[2]Faculty of Technology and Metallurgy, St.Cyril & Methodius University, MK-1000 Skopje, Republic of Macedonia

Abstract: Biodegradable poly (lactic acid) (PLA) based biocomposites reinforced with rice hulls were prepared by compression molding and their properties were compared to those of commonly used thermoplastic based-polymer, polypropylene (PP) containing the same reinforcements.

Rice hulls from rice processing plants represent renewable sources that could be utilized for production of new class of eco-materials. In this study, rice-hulls-filled poly (lactic acid) (PLA) biocomposites were prepared through addition of 5 wt. % PLA-grafted-MA (CA) for enhancement of adhesion between polymer matrix and natural filler. The composites containing 30% wt. rice hulls (RH) were prepared and the possibility of recycling and reuse of these biocomposites were investigated. For all biocomposites, the mechanical and thermal properties were analyzed and compared to those of commonly used thermoplastic based-polymer, polypropylene (PP) containing the same reinforcement. Thermal stability of neat biocomposites and of the new composites produced from recycled ones was practically unchanged. Utilization of the mixture obtained after the thermal-mechanical recycling of the whole biocomposite has resulted into composite with slightly increased flexural modulus and decreased flexural strength.

The obtained results have shown that rice-hull-filled poly(lactic acid) biocomposites could be recycled and utilized for production of new eco-materials with acceptable thermal and mechanical properties. Namely, the results for flexural strength and modulus of the recycled biocomposite samples are comparable to those of conventional formaldehyde wood medium density fiberboards used as construction elements for indoor applications.

Keywords: biocomposites, natural fiber-reinforced composites, poly(lactic acid), polypropylene, rice hulls, kenaf fibers, compression moulding.

Introduction

Recently the use of renewable resources for the production of polymer-based materials has attracted a growing attention, both in academia and industry, as a result of the increasing demand of environmental friendly materials [1]. The development of eco-composites (based on recyclable thermoplastics) as well as biocomposites (based on biodegradable polymers) and natural fibers as reinforcement has accelerated rapidly, primarily due to improvements in process technology and economic factors. These materials could allow complete degradation in soil or by composting process and do not emit any toxic or noxious component [2] [1]. Many investigations have been made on the potential use of different natural fibers as reinforcements for eco-composites (composite material with environmental and ecological advantages over conventional composites) and the results have shown that they exhibit good stiffness and promising properties [2], [3], [4], [5], [6], [1], [7], [8]. Natural fibers from renewable sources represent environmentally friendly alternative to conventional reinforcing fibers (glass, carbon, kevlar). Advantages of natural fibers over traditional ones are low cost, high toughness, low density, good specific strength properties, reduced tool wear

* *Correspondence to Vineta Srebrenkoska, Faculty of Technology, Goce Delčev University, "Krste Misirkov" b.b.* P. O. Box *201, 2000 Štip, Republic of Macedonia, phone: +389 32 550 000, fax: +389 32 390 700*
e-mail: Vineta Srebrenkoska (vineta.srebrenkoska@ugd.edu.mk)

(nonabrasive to processing equipment), enhanced energy recovery, CO_2 neutral when burned, biodegradability. The main drawback of natural fibers is their hydrophilic nature, that prevents their compatibility with hydrophobic polymers used as matrices for the production of composite materials, and therefore, different kinds of coupling agents have been used for improving interfacial adhesion between polymer matrices and natural fibers in order to enhance the physical and mechanical properties of the final products [9].

Depending on their performance, when they are included in polymer matrices, lignocellulosic fibers can be classified into three categories: wood flour particulates, which increase the tensile and flexural modulus of the composites, fibers (higher aspect ratio), that contribute to the improvement of the composite modulus and strength when suitable additives are used to optimize the stress transfer between the matrix and the fibers, and long natural fibers, with the highest efficiency among the lignocellulosic reinforcements. The most efficient natural fibers have been considered those showing high cellulose content coupled with a low microfibril angle, resulting in the best composite mechanical properties [10], [11].

On the other hand, the development of wholly biodegradable polymers and polymeric materials can play a fundamental role in helping to solve waste disposal problems [12]. Among biodegradable plastics, poly (lactic acid) (PLA), produced on a large scale from fermentation of corn starch to lactic acid and subsequent chemical polymerization, exhibit excellent mechanical properties, good heat resistance coupled with moldability, and recyclability. This polymer is characterized by its transparency, humidity and oil resistance. Pure PLA can degrade to carbon dioxide, water and methane in the environment over a period of several months up to 2 years, compared to other petroleum plastics needing longer periods [3], [4], [6]. The mechanical properties of PLA have been extensively studied as a biomaterial in medicine, but only recently it has been used as a polymer matrix in eco-composites [7], although its application is still limited by its relatively high price when compared to some other biodegradable polymers. Kenaf fibers have been already tested as natural reinforcement for polyolefines, but there is an even growing interest on the preparation of biocomposites [13], [14]. Xia et al. [9] investigated the use of PLA resin reinforced with kenaf fibers for the interior parts of its Prins hybrid car. In 2002 Cargill-Dow LLC started up a commercial polylactide plant, with the aim of production of PLA fibers for textiles and nonwovens, PLA film packaging applications, and rigid thermoformed PLA containers (http://www.cargilldow.com (accessed 2005).

Although PP could not be classified as a biodegradable polymer, this thermoplastic polymer takes an important place among eco-composites [11] primarily due to its recyclability, low cost and good price/performance ratio. Mohanty et al. has demonstrated that the natural fiber reinforced PP composites have potential to replace glass fiber-PP composites [10]. It has also been reported that PP can be effectively modified by maleic anhydride, providing polar interactions and covalent bonds between the matrix and the hydroxyl groups of cellulose fibers [15]. Visteon and Technilin developed flax/PP materials, R-Flax® based on low cost fibers. Tech-Wood International from the Netherlands announced Tech-Wood® eco-composite, suitable for construction elements [16]. Tech-Wood® eco-composite material contains 70% pine-wood fibers and 30% compatibilized PP.

In our previous study [17], [18], [19], compatibilization strategy was developed for both PLA and PP-based composites, and utilization of reinforcements from renewable sources for eco-composites has been investigated [20].

The purpose of this study was to investigate the recycling ability of the materials based on biodegradable PLA. PP-based composites were produced and their properties have been parallel determined, in order to compare their recycling behaviour and overall characteristics with those of PLA-based biocomposites. The rice hulls fillers were compounded with polymer matrix and coupling agent by melt mixing and then the obtained compounds were compression moulded. Also, the biocomposites were further granulated and blended twice by melt mixing, followed by compression moulding of new samples. Finally, the influence of the recycling process on the properties of composites was evaluated through the mechanical and thermal characterization of the composites.

This work is a follow up of the successfully finished ECO-PCCM project [21], in which eco-composites based on PLA, PHBV and PP were prepared and investigated in order to obtain new eco-friendly construction panels and elements for eco-houses [17], [19].

Materials and methods

Materials

PLA, produced by Biomer, Krailling – Germany and isostatic PP, Moplen X30S, kindly supplied by Basell Polyolefins (Ferrara, Italy), were used as matrices for bio- and eco-composites. Rice hulls from agricultural waste were kindly supplied by Rice Institute from Kocani, Macedonia. Before mixing, rice hulls (RH) were vacuum-dried for 24h to adjust their moisture content to 1-2 wt%. Maleic anhydride-grafted PLA (MAPLA) and maleic anhydride-grafted PP (MAPP), KA 805 (Basell Polyolefins Ferrara, Italy), were used as coupling agents (CA) and they have been added to PLA and PP during the reactive blending.

Compounding of composite materials

The preparation of the composite compounds has been preformed by melt mixing, in a Haake Rheocord 9000 batch mixer (New Jersey, USA). First, the polymer and coupling agent were mixed for 3 min at 185^{o}C and 175^{o}C, respectively for PP and PLA based composites; then 30 wt% of fillers (rice hulls, RH)/fibers (kenaf, K) were added and the mixing proceeded for further 10 min at the same temperature. The mixing speed was progressively increased during the mixing, up to 64 rpm (3 min with a mixing speed of 8 rpm, then 4 min at 38 rpm and finally 3 min at 64 rpm). Then the obtained composites were cut into granules and reprocessed under the same preparation conditions (recycling process). This recycling process was carried out twice.

The codes of the samples obtained are shown in Table 1.

Table 1. Codes of composite samples produced by compression molding using neat or recycled polymer as a matrix, and produced from wholly recycled composites

Codes	Description	Matrix (wt%)		Fiber/Filler		Coupling agent	
		Type	Content (wt%)	Type	Content (wt%)	Type	Content (wt%)
PLA/RH	Neat	PLA	70	Rice hulls	30	/	/
PLA/RH/CA	Neat	PLA	65	Rice hulls	30	MAPLA	5
PLA/RH/CA (x1)	Composite recycled once						
PLA/RH/CA (x2)	Composite recycled twice						
PP/RH	Neat	PP	70	Rice hulls	30	/	/
PP/RH/CA	Neat	PP	65	Rice hulls	30	MAPP	5
PP/RH/CA (x1)	Composite recycled once						
PP/RH/CA (x2)	Composite recycled twice						

Compression moulding

The samples for mechanical testing were fabricated by compression moulding. The pellets obtained after melt mixing of starting materials were put in a moulding frame with desired dimensions and compression moulded at T= 175^{0}C for PLA based composites and T= 185^{0}C for PP based composites, both for 10 minutes, with a progressive increase of pressure from 50 to 150 bar. Finally, the press was cooled using a cold water flow. Sheets with a thickness of about 5 mm were obtained.

Methods

Mechanical and thermal properties of the composites such as impact resistance (Charpy impact test according ASTM D 256), compression strength (ASTM D 695), flexural strength and the modulus (ASTM D 790) were determined. For all mechanical tests, the universal testing machines (Schenk and Frank, Germany) were used. The thermal stability of composites was analyzed using a Perkin Elmer Pyris Diamond Thermo gravimetrical Analyzer (TGA). About 10 mg of each sample was heated from 50^{o}C to 600^{o}C at heating rate of 20^{o}C/min under nitrogen flow rate (25 ml/min). Morphological analysis was performed by using a JEOL scanning electron microscope (SEM), on cryogenically fractured surfaces of composite samples. Before the observation, the specimens were metallized with a gold/palladium coating in a Polaron Sputtering.

Results and discussion

Mechanical analysis

In our previous studies we investigated the properties of a new class of biodegradable PLA-based composites reinforced with kenaf fibers produced with or without compatibilizing agent [12]. Also, the effects of compatibilization on the performance of PHBV-based biocomposites were evaluated [18], [22]. The main goal of this work was the preparation and characterization of PLA-based biocomposites reinforced with rice hulls, with particular attention to possibility of their reuse. For this purpose

PLA biocomposites and PP eco-composites were first prepared by a proper in situ reactive compatibilization, a strategy inducing a strong interfacial fiber/polymer adhesion and thus resulting in improvement of the mechanical properties [23].

The coupling agents used for compatibilization are constituted from PP and PLA segments (the same as the polymer matrices) and by MA groups grafted onto PP and PLA segments, which become reactive with respect to hydroxyl groups present on the reinforcement surface. In this way, physical and/or chemical interactions between hydroxyl and maleic anhydride groups, generated during the mixing, are responsible for *in situ* formed grafted species that can act as effective compatibilizer for the PP and PLA/natural filler reinforcement composites [24], [25].

Our task was to examine the recycling behaviour of the biocomposite itself by the analysis of the properties of re-processed composites produced from the recycled ones. In order to evaluate the response of composites to the recycling process in terms of mechanical properties, the obtained materials were successively reprocessed as reported in the experimental session. Table 2 shows the summary of the flexural properties for neat and recycled rice hulls-based composites. Incorporation of rice hulls into PLA matrix produced an increase in the flexural modulus, reaching 3,0 GPa for composite PLA/RH (70/30wt.%), and a drop in the stress at a peak of around 57%. However, the presence of a coupling agent in PLA/RH composites doubled the stress at the peak in flexure value. Composite PLA/RH/CA (65/30/5wt.%) exhibited stress at the peak in flexure of almost 29 MPa, which is close to the value displayed by pure PLA. Modulus in flexure increased in the presence of coupling agent. The extent of the modulus improvement is correlated to the filler/matrix interfacial adhesion, thus justifying the highest modulus value obtained in the presence of reactive coupling agent. Flexural strength of PLA/RH/CA (65/30/5wt.%) recycled composites decreases for about 50% after recycling, although the flexural modulus is practically unchanged. As reported in literature, the recycling process of polymer/fiber composites frequently induces a decrease in the physical properties of composites. The extent of this decrease is strictly correlated to the decline in the molecular weight of the polymer matrix and to the deterioration of fibers/fillers in terms of length caused by repeated kneading [26].

Table 2. Flexural properties of neat and recycled PLA - based biocomposites

Sample	Stress at peak, MPa	Modulus, GPa
PLA	32,0 ± 2,8	2,4 ± 0,14
PLA/RH (70/30wt.%)	13,9 ± 3,4 (-56,6 %)[a]	3,0 ± 0,21 (+25,0 %)[a]
PLA / RH /CA (65/30/5wt.%)	28,8 ± 6,6 (-3,5 %)[a]	3,2 ± 0,18 (+33,3 %)[a]
PLA/RH /CA (x1) (65/30/5wt.%)	12.1 ± 4,8 (- 58,0 %)[b]	3,24 ± 0,38 (+1,25 %)[b]
PLA/RH /CA (x2) (65/30/5wt.%)	10,7 ± 2,5 (- 62,8 %)[b]	3,32 ± 0,18 (+ 3,75 %)[b]

[a] In brackets are the percentage changes of the corresponding property, compared to the value for neat PLA

[b] In brackets are the percentage changes of the corresponding property, compared to the value for neat composite PLA/RH/CA

Within the framework of this investigation, the recycling behaviour and overall characteristics of PLA-based biocomposites were also compared to composites based on commonly used thermoplastic polymer, polypropylene (PP) containing the same reinforcement. For that aim, PP-based composites were produced and their recycling behaviour and overall properties have been determined. Although PP could not be classified as a biodegradable polymer, this thermoplastic polymer takes an important place among eco-composites [11] primarily due to its recyclability, low cost and good price/performance ratio. Mohanty et al. has reported that PP can be effectively modified by maleic anhydride, providing polar interactions and covalent bonds between the matrix and the hydroxyl groups of cellulose fibers [10].The obtained values for PP-based composites for flexural strength and modulus are similar with those of neat PP (Table 3). The recycling processes for these composites induce a slight decrease of the flexural strength after the second recycling (about 5%) and an increase of the flexural modulus (about 20%). As expected, the PLA-based biocomposites have lower mechanical properties than the PP - based ones, but significant deterioration of flexural properties is seen in recycled PLA based biocomposites. Nevertheless it is well known that polyolefins are less sensitive to the reprocessing than other polymers such as polyesters. Therefore, unless recycling processes can induce beta-scission in the polymer matrix, the possible molecular weight decrease due to the reprocessing does not seem to significantly affect the mechanical properties of the PP based composites reinforced with rice hulls. Concerning PLA-based biocomposites, our further investigations are directed towards the possibilities of improving their stability during re-processing cycle, which will be a subject of our future publication.

Table 3. Flexural properties of neat and recycled PP - based composites

Sample	Stress at peak, MPa	Modulus, GPa
PP	51,5 ± 5,5	1,1 ± 0,12
PP/RH (70/30wt.%)	31,6 ± 2,4	0.9 ± 0,31
PP /RH /CA (65/30/5wt.%)	42,6 ± 3,4	1,9 ± 0,08
PP/RH /CA (x1) (65/30/5wt.%)	44,8 ± 3,0	1,88 ± 0,16
PP/RH /CA (x2) (65/30/5wt.%)	38,5 ± 7,2	1,91 ± 0,06

Oksman et al. [6] has studied the recycling properties of the PLA/kenaf composite. The physical properties and molecular weight were held close to 90% of that of the initial PLA/kenaf composites. The physical properties of the PLA/kenaf composite probably can be kept constant by the adjustment of the ratio of the initial PLA/kenaf composite and the recycled one. Sanadi et al. [27] has studied the possibility of using highly filled agro-based fiber thermoplastic composites for furniture, automotive and building applications. They have shown that the performances of thermoplastic based composites are better than most of wood particle, low and medium density fiberboards. For our systems, a comparison of flexural properties of commercially available formaldehyde-based wood composites [27] and 30% filled PP/rice hulls and PLA/ rice hulls composites produced by compression molding is given in Table 4.

The investigated composites show flexural properties comparable to conventional formaldehyde-based fiberboards [27]. Moreover, these parameters remain similar to those of formaldehyde-based wood composites also after the recycling processes.

Table 4. Comparison of flexural properties of commercially available formaldehyde-based wood composites (Sanadi, et al.,2001) and compatibilized PP/Rice hulls and PLA/Rice hulls biocomposites produced by compression molding

Sample	Flexural strength range (MPa)		Flexural modulus range (GPa)	
	low	high	low	high
High-density fiberboards [28] (commercial)	38	69	4.48	7.58
Medium-density fiberboards [28] (commercial)	13.1	41.4	2.24	4.83
PP/RH	42.6 (3.4) [a]		1.94 (0,08) [a]	
PLA/RH	28.8 (3.1) [a]		3.0 (0.09) [a]	

[a] Standard deviations are in brackets for the PP/rice hull and PLA/rice hull biocomposites

Since the industrial manufacturing of the composites proceeds mainly in nonisothermal regime, analysis of the crystallization parameters and crystallization behavior of the polypropylene based composites is especially important from a practical point of view. Generally, for composites based on semicrystalline polymers, the crystallinity is an important factor that determines the stiffness and fracture behavior of the matrix [22]. The crystallinity depends upon processing parameters, e.g. T_c, cooling rate, nucleation density and annealing time [18], [19]. It should be mentioned, that, in our previous paper it was reported that the addition of rice hulls or kenaf fibers to polylactic acid and polypropylene resulted in an increased crystallization temperature and accelerated crystallization process due to the "nucleating" effect of the filler [26]. This behavior could advantageously affect the industrial processing of the composites.

Thermal stability of PLA-biocomposites and their behaviour after recycling

Thermal stability of biocomposites produced from neat and recycled matrix, as well as from wholly recycled composite, was analyzed by TGA/DTG, and the results were compared to those obtained for PP-based eco-composites.

Results from the thermogravimetric analyse of PLA, rice hulls and the biocomposite PLA/RH/CA (65/30/5wt.%) are presented in figure 1(a) and table 5.

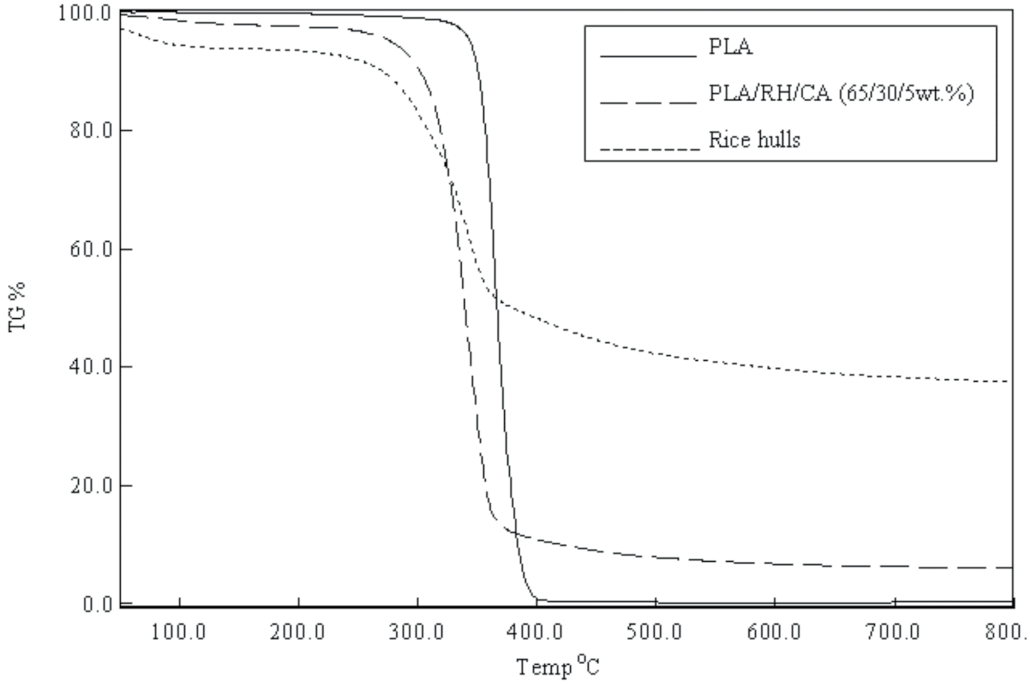


Figure 1a. Thermogravimetric curves of PLA, rice hulls and PLA/RH/CA (65/30/5wt.%) biocomposites: weight loss (%) versus temperature

Table 5. Thermal stability of PLA, rice hulls and biocomposite PLA/RH/CA (65/30/5wt.%)

T (°C)	Weight loss (%)		
	Rice hulls	PLA/RH/CA (65/30/5wt.%)	neat PLA
50	2,7	0,5	0
100	5,6	1,4	0
150	8	3,2	0,5
290	14	6,9	0,9
310	20,6	13,7	1,2
330	29,7	33,5	2,1
350	43	69,8	9,5
370	49,1	86,9	61,3
390	51	88,7	95,7
410	52,6	89,7	99,6
600	60,3	93,3	100

As evident, rice hulls undergo two-step weight loss process: below 110°C weight loss resulted from the evaporation of absorbed moisture and in the temperature range between 170 and 500°C - from the degradation of rice hulls three major constituents. The lignocellulosic materials are chemically active and they are thermo-chemically decomposed between 150 and 500°C: hemicellulose mainly between 150 and 350°C, cellulose between 275 and 350°C, and lignin between 250 and 500°C [28]. Ash in the rice husk (12%) is mainly composed of silica (~96%), and the amount and distribution of silica in the rice husk is likely to be an important factor in determining the composite product properties [29], [28]. PLA gradually loses 10%

of its weight till 350°C, and afterward suffers almost complete weight loss in a temperature interval from 350°C till 400°C. PLA based composite PLA/RH/CA (65/30/5wt.%) loses 10% of its weight till 300°C, followed by ongoing 75% weight loss till 360-365°C, after that, weight loss continues with slower degradation rate. It should be noted that at the temperature of 600°C rice hulls exhibit high residual weight of 39,7%. These findings are in accordance with the finding of Lee et al. [30], that thermal stability of PLA/bamboo fibre composites is lower than thermal stability of neat PLA matrix.

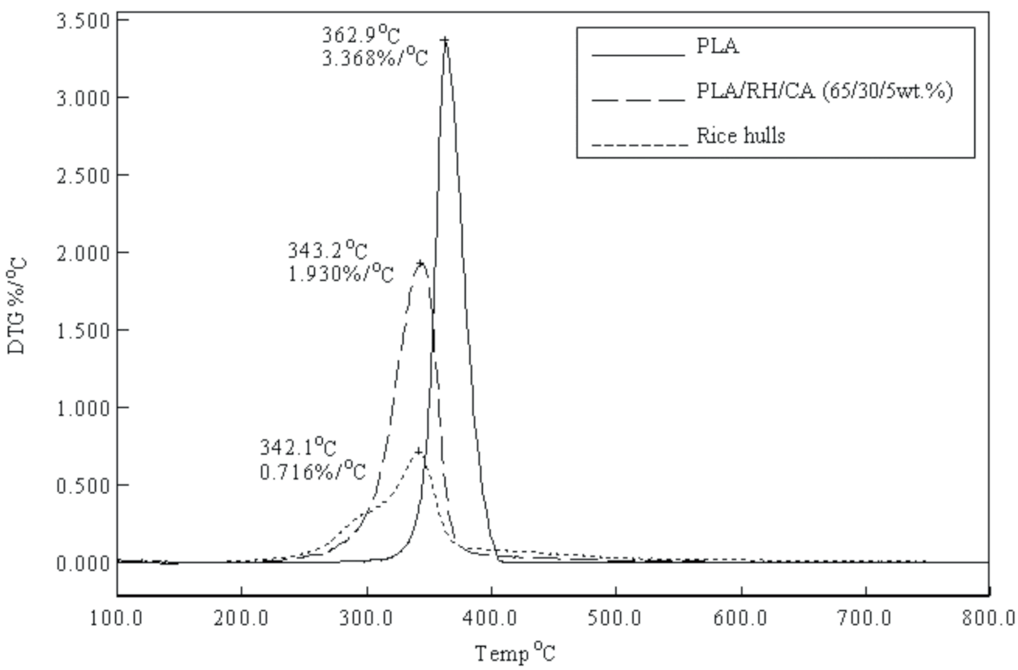


Figure 1b. Derivative thermogravimetric curves of PLA, rice hulls and PLA/RH/CA (65/30/5wt.%) biocomposites: derivative weight loss (% / °C) versus temperature

Derivative thermogravimetric curves for neat PLA, rice hulls and their composite PLA/RH are presented in figure 1 (b). Maximum weight loss rate for PLA (3,37%/°C) is reached at 362,9°C, and for rice hulls weight loss rate is uppermost (0,72 %/°C) at 342,1°C. Composite PLA/RH/CA (65/30/5wt.%) exhibits maximum weight loss rate of 1,93 %/°C at 343,2°C, a temperature almost 20°C lower than the corresponding one for neat PLA, proving again the previous finding of composites' insignificantly lower thermal stability.

We investigated thermal behavior of the composites produced from wholly recycled ones, in terms of their sustainability values. Thermal degradation of once and twice recycled PLA/RH/CA (65/30/5wt.%) biocomposites proceeds in a single step, and occurrs at 323,8°C (PLA/RH/CA x1) and 319,5°C (PLA/RH/CA x2), respectively, and the TG-curves have the same behavior. The recycled composites have shown a lower degradation temperature (less than 20°C), exhibiting a decrease of the degradation temperature (for about 20°C) after the second recycling.

Table 6. Thermal stability of bio- and eco-composites produced from recycled matrices and recycled composites, as determined by TGA at residual weight of 90% (Td_{90}), 50% (Td_{50}), and 10% (Td_{10})

Sample	Td_{90} (°C)	Td_{50} (°C)	Td_{10} (°C)
PLA/RH/CA (65/30/5wt.%)	308,2	341,3	534,2
PLA/RH/CA (x1) (65/30/5wt.%)	294,4	323,8	517,3
PLA/RH/CA (x2) (65/30/5wt.%)	289,1	319,5	501,1
PP/RH/CA (65/30/5wt.%)	344,43	411,21	452,17
PP/RH/CA (x1) (65/30/5wt.%)	336,7	409,9	471,0
PP/RH/CA (x2) (65/30/5wt.%)	322,6	389,0	455,3

The results obtained from thermal analysis have shown that biocomposites based on PLA and rice hulls as reinforcement could be reused by recycling and re-forming, and this process is more convenient than the recycling and re-use of the matrix itself.

Conclusion

On the basis of the results obtained for the mechanical properties and thermal behavior of PLA-based biocomposites produced from: neat and from wholly recycled composite, the following conclusions can be drawn: the rice hulls representing agricultural waste derived from rice-production could be used as a biodegradable eco-friendly filler, rather to minimize environmental pollution and cost of the final product than as a reinforcement of PLA matrix. Introduction of 5 wt.% PLA-g-MA improved the strength of PLA based composites with 30 wt.% rice hulls, which is a result of enhanced interfacial adhesion. The flexural properties of wholly recycled biocomposites are very close to those of the neat ones. Thermal stability of the biocomposites produced by re-processing from wholly recycled composites is not significantly affected by the first recycling process. Therefore, it could be recommended as a procedure for further utilization of these materials after their life time. The biodegradable PLA based biocomposites represent a good potential for utilization after recycling. The obtained results for flexural strength and modulus of the recycled biocomposite samples are comparable to those of conventional formaldehyde wood medium density fiberboards used as construction elements for indoor applications.

Our further analyses are concerned with investigation of the possibilities of improving their stability during the re-processing cycle.

Acknowledgements

This work is a follow-up of a successfully finished ECO-PCCM project which was financially supported by EU FP6-INCO-WBC program [21]. The production and characterization of the compressed polymer eco- and biocomposites were carried out in “11 Oktomvri-Eurokompozit” - Prilep, Macedonia. Thermal analysis was performed at the Institute of Chemistry and Technology on Polymers-ICTP-CNR, Italy. The authors are very grateful to all these institutions for their support in fulfillment of this research.

References

[1] Chen Y., Chiparus L.S., Negulescu I., Parikh D.V., Calamari T.A. (2005). Natural Fibers for Automotive Nonwoven composites. J. of Ind. Text. 35, 47-61.

[2] Mieck K.P., Nechwatal A., Knobeldorf C. (1994). Potential applications of natural fibres in composite materials. Melliand Textilberichte. 11, 228-330.

[3] Heijenrath R. Peijs T. (1996). Natural-fibre-mat-reinforced thermoplastic composites based on flax fibers and polypropylene. Advanced Composites Letters. 5(3), 81-5.

[4] Oksman K. (2000). Mechanical properties of natural fibre mat reinforced thermoplastics. Appl. Comp. Mat. 7, 403-14.

[5] Oksman K. (2001). High quality flax fibre composites manufactured by the resin transfer moulding process. Journal of Reinforced Plastics and Composites. 20(7), 621-37.

[6] Oksman K., Skrifvars M., Selin J.F. (2003). Natural fibers as reinforcement in polylactic acid (PLA) composites. Composites Science and Technology. 63, 1317-24.

[7] Serizawa S., Inoue K., Iji M. (2006). Kenaf-fiber-reinforced poly(lactic acid) used for electronic products. Journal of Applied Polymer Science. 100, 618-24.

[8] Seung-Hwan Lee, Siqun Wang (2006). Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent. Composites: Part A. 37, 80-91.

[9] Xia Z., Curtin W.A., Okabe T. (2002). Compos. Sci. Technol. 62, 1279-91.

[10] Mohanty A.K., Drzal L.T., Misra M. J. (2002). Adhes. Sci. Technol. 16, 999-1023.

[11] Yang H.S., Kim D.J., Lee J.K., Kim H.J., Jeon J.Y., Kang C.W. (2004)b. Possibility of using waste tire composites reinforced with rice hulls as construction materials. Bioresource Technol. 95, 61-5.

[12] Avella M., Bogoeva-Gaceva G., Buzarovska A., Errico M.E., Gentile G., Grozdanov A. (2008). Poly (lactic acid)-based biocomposites reinforced with kenaf fibers. J. Appl. Poly. Sci. 108, 3542-51.

[13] Chen H-L., Porter R.S. (1994). Journal of Applied Polymer Science. 59, 1329-42.

[14] Karnani R., Krishnan M., Narayan R. (1997). Polymer Engineering and Science. 37, 476-94.

[15] Keener T.J., Stuart R.K., Brown T.K. (2004). Compos. A. 35, 357-81.

[16] Netravali A.N., Chabba, S. (2003). Mater. Today. 6(4), 22-39.

[17] Bogoeva-Gaceva G., Grozdanov A., Buzarovska A. (2005). Eco-friendly polymer composites based on polypropylene and kenaf fibers. Proceedings of 3rd International Conference on Eco Composites. Royal Institute of Technology, Stockholm, Sweden, june 20-1.

[18] Avella M., Bogoeva - Gaceva G., Buzarovska A., Errico M.E., Gentile G., Grozdanov A. (2007). Poly (3 - hydroxybutyrate - co - 3 - hydroxyvalerate) - based biocomposites reinforced with kenaf fibers. J. Appl. Polym. Sci. 104, 3192-200.

[19] Dimzoski B., Bogoeva-Gaceva G., Gentile G., Avella M., Errico M.E., Srebrenkoska V. (2008). Preparation and characterization of poly(lactic acid)/rice hulls based biodegradable composites. J. Polym. Eng. 28, 369-84.

[20] Grozdanov A., Bužarovska A., Bogoeva-Gaceva G., Avella M., Errico M.E., Gentile G. (2006). Rice straw as an alternative reinforcement in polypropylene composites. Agronomy for Sustainable Development. 26, 251-5.

[21] ECO-PCCM, FP6-INCO-CT-2004-509185.

[22] Grozdanov A., Bužarovska A., Bogoeva-Gaceva G., Avella M., Errico M.E., Gentile G. (2007). Nonisothermal crystallization of kenaf fiber/polypropylene composites. Polymer Engineering and Science. 47, 745-9.

[23] Dimzoski B., Bogoeva-Gaceva G., Gentile G., Avella M., Grozdanov A. (2009). Polypropylene based eco-composites filled with agricultural rice hulls waste. Chem. Biochem. Engineering Quarterly. 23 (2), 225-20.

[24] Bogoeva-Gaceva G., Grozdanov A., Buzarovska A. (2006). Nonisothermal crystallization of maleic anhydride grafted PP: comparison of different kinetic models. Proceedings of 5th International Conference of the Chemical Societes of South-East European countries ICOSECS-5, Ohrid, Macedonia, september 10-4.

[25] Bogoeva-Gaceva G., Grozdanov A., Dimzoski B. (2007). Analysis of the reaction of modified polypropylene in melt. Proceedings of European Polymer Congress EPF, Portoroz, july 2-6.

[26] Buzarovska A., Bogoeva-Gaceva G., Grozdanov A., Avella M. (2006). Crystallization behavior of polyhydroxybutyrate in model composites with kenaf fibers. Journal of Applied Polymer Science. 102 (1), 804-9.

[27] Sanadi A.R., Hunt J.F., Caulfield D.F., Kovacsvologyi G., Destree B. (2001). High fiber-low matrix composites: kenaf fiber/polypropylene. Proceedings of 6th International Conference on Woodfiber-Plastic Composites, Madison, Wisconsin, may 15-6.

[28] Kim H.S., Yang H.S., Kim H.J., Park H.J. (2004). Thermogravimetric analysis of rice husk flour filled thermoplastic polymer composites. J. Therm. Anal. Calorim. 76, 395-404.

[29] Sanadi A.R., Caulfield D.F., Jacobson R.E., Rowell R.M. (1995). Renewable agricultural fibers as reinforcing fillers in plastics: Mechanical properties of kenaf fiber-polypropylene composites. Indust. Eng. Chem. Res. 34, 1889-96.

[30] Lee S.H., Wang S. (2006). Composites Part A. 37, 80-91.

Recived: 01.03.2011.
Accepted: 20.06.2011.

Original scientific paper UDC: 616.8-056.83:316.624

Cultural Dimension of Sustainable Development as a Presumtion of Local Communities Development[1]

Vesna Miltojević[1], Ivana Ilić-Krstić
University of Niš, Faculty of Occupational Safety in Niš

Abstract: The term "sustainable" can be found in both science and practice. As a global concept of development, it was accepted at the Conference in Rio de Janeiro in 1992 in order to overcome and find a possible way of dealing with problems connected to the development of contemporary civilization. Three dimensions of sustainable development are usually mentioned: economic, social and ecological. The paper points out the significance of the fourth dimension – cultural dimension, which is not only significant for reaching development in the real sense of the world, but it also represents the basis for the development of local communities. The cultural dimension respects the particularities of local communities and emphasizes the maintenance of the cultural and national variety which is of special significance for multicultural societies.

Keywords: dimensions of sustainable development, cultural dimension of sustainable development, sustainable development, variety.

Introduction

Sustainable development as a model of social development at a global level is becoming more significant along with more and more distinct manifestation of negative anthropogenic influence on the environment. The 1950s were the beginning of pointing out the necessity to reexamine the current model of development which rested on the profit-oriented industry and the anthropocentric view of the world, that is, as Plumwood states, on arrogant culture [1]. Taking into consideration warnings against the rapid crash of the industrial system and depletion of natural resources, the search for a new model of development, shaped through the concept of sustainable development, began.

One of the first definitions of sustainable development, which rests on harmonizing economic development with a need to preserve the environment and intergenerational solidarity, was given in the so-called Brutland report, known as *Our Common Future*. In the report, sustainable development is defined as "the development used to meet the present needs, so as not to jeopardize future generations to satisfy their own needs. Basically, sustainable development is a process of changes within which the exploitation of resources, direction of investments, orientation of technological development and institutional changes are in harmony and enable the use of present and future potentials so as to satisfy human needs and aspirations" [2]. Regardless of the polemics caused by the definition itself, because of the insufficient operationalization of the terms need and aspiration, the report is significant because it stresses problems such as poverty, violation of ecological balance and a need for the protection of the environment, that is, it points out a need to harmonize the socio-economic development with the possibilities and capacities of the environment while avoiding economic, social and ecological risks and crises. What followed were numerous efforts to define this model of development more precisely by numerable scientists (for example Hauff, Kirn, Magda), but also by international organizations and forums (for example World Conservation Union, World Bank). Thus, depending on the approach (economic, ecological, sociological, etc), and in order to operationalize

1 Tel: +381 63 104 25 07, fax: +381 018 249 962, e-mail: vmiltojevic@yahoo.com

the definition which is the precondition for building strategies of sustainable development, this model of development is determined as the process of changes by which "the use of resources, structure of investments, orientation of technological advancement and institutional structure arrive at agreement with the future and present needs" [3], or as the development which "focuses on people and its aim is to improve the quality of human life. Sustainable development is based on protection, so that it is conditioned by the need to respect the capacity of nature, in order to provide resources and services needed for life" [4].

Considering the fact that sustainable development was accepted as a model of development at a global level, at the UN Conference in Rio de Janeiro in 1992, but that it is necessary to apply it to the local level, the question of the relationship between global and local seems interesting. Most frequently the relationship between global (which refers to the whole world) and local (something limited in space) is seen dualistically through the valuation-hierarchical view of the world, whereby global is favorized. Modernity, development and universality relate to global, and tradition, underdevelopment, particularity relate to local. According to this approach, global is universal and all that is local has to conform and subordinate to it. However, accepting such an interpretation of global and local would lead to the unification and loss of the particularity of special areas. Thus, the global-local relationship should be considered and interpreted from the point of their inseparable interconnection. Only in this way it is possible to reach real development which, according to Major, has to be in accordance with moral and cultural aims rooted in the historical heritage of every people [5], and sustainable development will not be something abstract, but it will be perceived and placed into local frameworks in the right way, because local space, as Korff [6], writes, is structured by the organization which finds specific (local) knowledge important.

Dimensions of Sustainable Development

Taking into consideration the definition of sustainable development given in *Rio Declaration of the Environment and Development*, which primarily highlights "people's right to lead a healthy and productive life in accordance with nature" and intergenerational responsibility, but also the necessity to harmonize development with the protection of the environment, the eradication of poverty, as well as the necessity for cooperation which would lead to economic growth, sustainable development and the protection of the environment [7], a large number of authors emphasize the connection between economic growth and the protection of the environment. Thus sustainable development is understood as "a form of social and structural social transformation which respects the relationship between economic growth and non-renewable resources" [8], that is, as a strategy of development managed using all basic means, natural resources, as well as financial means in order to increase long-term wealth and welfare [9], as a concept which reconciles and harmonizes economic with ecological aims by means of a complementary overview of economic and ecological interests and integral economic development [10]. In that sense, three dimensions of sustainable development are emphasized: economic, social and ecological, and there is a demand for "a redefinition of economic growth, a reasonable use of natural resources and the increase in the quality of production; eradication of poverty and satisfaction of basic needs of the population (job, food, energy, water supply, housing and health); acceptable population growth; preservation of natural resources and increase in variety by means of maintaining ecosystems and monitoring the influences of economic activities on the environment; technological changes and the control of technological resources", but also the decentralization of power and active participation of citizens in the decision-making process, making national and international regulations considering the environment and development [11]. The three-dimensional conception of sustainable development is most often represented in the form of a tripod, whereby the need for an integral overview of these three dimensions of development and equality of all three elements are emphasized, because, as Hart states [12], the solution to the problem is in only one element leading to a problem or worsening the already existing problems in other two elements, contrasting interests and short-term solutions and profit by ignoring the long-term results.

There are authors who, starting from sustainable development as integral development, consider that sustainable development should not be reduced to three dimensions in any way, and thus they introduce the fourth dimension as well. Some consider that it is culture [13], while others suggest politics or institutions. Thus Lay connects social and cultural dimensions and suggests three more: bio-ecological, economic and political dimensions [14], while Spangenberg, beside economic, social and ecological dimensions, mentions the institutional dimension as well [15]. Accepting di Castri's attitude that if we want to reach sustainable development, it is necessary to harmonize four backbones of sustainable development: economic, ecological, social and cultural, we remind ourselves of its metaphor of a Renaissance chair. "Sustainable development can function only when four backbones of development – economic, social, cultural and the environment – are of equal importance and strength, with a strong mutual connection and interdependence provided with an adjustable institutionalized basis. If one leg of the chair is shorter or lower than the others, there is no sitting comfortably, no sustainability /…/" [13].

Culture and Sustainable Development of Local Communities

Not diminishing the significance of the standpoint that the fourth pillar of sustainable development is politics or institutions, we still consider that the fourth pillar is culture, because, in fact, culture represents an agglomeration of material and spiritual creations human activity has made in order to improve and prolong human life. The cultural dimension [13], primarily includes new ethics and behavior, but also the respect for and nurture of a religious and cultural variety. In effect, as Hawkes [16], claims, the fourth pillar of sustainability – culture contributes to the improvement of the quality of life and includes the nurture of partnership, respect and an exchange between the different aspirations of government, business, art organizations and citizens. In that sense, this pillar points to the necessity to create and develop the framework for the evaluation of the influence that culture has on the environment, on economic and social decisions. Keith Nurse [17], has a similar attitude, according to which culture is the key element of sustainable development. According to her, culture shapes what we consider to be development and determines how people act in the world. The cultural dimension of sustainable development includes "the ability to preserve cultural identity along with enabling changes in accordance with cultural values" [18], it contributes to a cultural variety which is equal to the value of biodiversity, identification and protection of cultural identities and the promotion of cultural particularities enabling the transition to sustainable development [17].

The necessity "to lower" the concept of sustainable development from global to regional, national level and the level of local communities, as well as the need to consider sustainable development through the cultural dimension also, were pointed out in the article 22 of Rio declaration of the environment and development. "Indigenous people and their communities, as well as other local communities, have a vital role in managing the protection of the environment and in development because of their knowledge and traditional way of life" [7].

However, regardless of pointing to the necessity to perceive sustainable development through the cultural dimension as well, strategic documents made at the level of national states base their strategies mostly on three pillars of sustainable development. However, there are exceptions. New Zealand Ministry of Culture and Heritage, in its documents, emphasizes that the local authority is responsible for promoting "social, economic, ecological and cultural welfare of the community for the present and the future", and points out the mutual connection between all four aspects of welfare, whereby the welfare of everyone is in the center, and culture represents the key dimension of sustainability because it primarily includes the right of individuals to freely express their identity, history, heritage, tradition and participate in cultural, but also in recreational activities [17]. The cultural dimension of sustainability can also be found while analyzing the life of Aborigines in the region of Vancouver. Cardinal and Adin place the health of people, nation and country into the center of sustainability, and believe that all four dimensions of sustainable development are necessary for the realization of these [19]. Analyzing the specificity of Aborigines' lives, taking into consideration the tradition which connects culture and the family, these authors suggest the indicators of cultural sustainability in the region. At the same time, the given indicators are not perceived as static, but as developmental, with regard to the interconnection and interaction between the dimensions of sustainability and a constant change in society.

In order for sustainable development not to be something abstract for the largest number of people, something that stifles local, that is, in order to realize full development for real, it is necessary to plan development through the cultural dimension as well at the level of local communities. In that sense, it is necessary to explore cultural (material and spiritual) heritage of local communities and tradition, along with finding possibilities for these to be a part of the strategies of the local sustainable development.

Conclusion

Introducing the cultural dimension of sustainable development is especially significant while planning the development in multicultural and multinational environment, because only when we accept cultural, natural and all other specificities and particularities of the local community and when we harmonize the aims of development with them, it is possible to realize full development. Besides, this dimension contributes to the realization of basic human rights and the establishment of permanent peace.

In the end, it is worth mentioning that unlike other three dimensions of sustainable development, the cultural dimension has no generally accepted set of indicators which would follow the degree of its feasibility. One of the limiting factors is the interdependence of the dimensions of the sustainable development, especially the cultural and social ones, and the other is the fact that every local community has its own characteristics. Nevertheless, the first steps were made after the Agenda 21 for culture was established in Porto Alegro in 2004 at the Forum of local self-governments for including citizens in the decision-making processes, through recommendations to UNDEP to include cultural indicators while calculating the human development index (HDI) and to the UN sustainable development section to develop the cultural dimension of sustainability. However, until the generally accepted indicators are adopted, it is necessary for every local community to determine its own indicators, whereby we should bear in mind the current state of affairs in the community, historic heritage, tradition and respect for basic human rights. Cultural sustainability of the local community could be monitored, for example, through demographic data, legislation, contents of radio and TV shows, printed media, concern over cultural heritage, participation and practice of customs, but also through the compatibility of production activities with traditional activities.

References

[1] Plumwood V. (2002). Environmental Culture: The ecological Crisis of reason. New York: Routledge.

[2] World Commission on Environment and Development (1987). Our Common Future. Oxford.

[3] Hauff V. (2004). The German Council for Sustainable Development. Greenleaf Publishing Limited.

[4] IUCN, UNEP, WWF. (1991). Caring for the Earth: A Strategy for Sustainable Living. Switzerland: Gland.

[5] Major F. (1991). Sutra je uvek kasno. Beograd: Jugoslovenska revija.

[6] Korff R. (2003). Local Enclosures of Globalization, The Power of Locality. Dialectical Anthropology, 27, 1-18.

[7] Rio deklaraciji o životnoj sredini i razvoju. (1997). Beograd: Savezno Ministarstvo za zaštitu životne sredine.

[8] Pearce D.W. et al. (1990). Sustainable Development: Economics and the Environment in the Third World. London: Earthscan Publications.

[9] Repetto R. (1986). World Enough and Time – Successful Strategies for Resource Management. New Haven: Yale University Press.

[10] Mileusnić V. (1995). Ekologija i globalni privredni razvoj. Direktor, 4-5, 30-7.

[11] Orboi M.D. et al. (2010). Sociological dimensions of sustainable development. Research Journal of Agricultural Science, 42(3), 749-55.

[12] Farrell A. and M. Hart (1998). What Does Sustainability Really Mean? The Search for Useful Indicators. Environment 40, 4-9, 26-31.

[13] Di Castri F. (1995). Came up with a good metaphor: "The Chair of Sustainable Development". Nature & Resources, 3(3), 2-7.

[14] Lay V. (ur.) (2007). Razvoj sposoban za budućnost − prinosi promišljanju održivog razvoja. Zagreb: Institut društvenih znanosti Ivo Pilar.

[15] Hak T. et al. (2007). Sustainability Indicators: an Scientific Assessment. London and Washington: IslandPress.

[16] Hawkes J. (2001). The Fourth Pillar of Sustainability: Culture's Essential Role in Public Planning. Australia: Common Ground Publishing, Pty Ltd.

[17] Nurse K. (2006). Culture as the Fourth Pillar of Sustainable Development. <http://www./SARD/Cultureas4thPillarSD.pdf>. Accessed 25.02.2011.

[18] Social capital formation and institutions for sustainability. (1998). Sustainable Development Research Institute. Workshop. Vancouver.

[19] Duxbury N. and E. Gillette (2007). Culture as a Key Dimension of Sustainability. Canada: Centre of Expertise on Culture and Communities.

(Endnotes)

Prepared as a part of the project *Sustainability of the Identity of Serbs and National Minorities in the Border Municipalities of Eastern and Southeastern Serbia* (179013), conducted at the University of Niš – Faculty of Mechanical Engineering, and supported by the Ministry of Science and Technological Development of the Republic of Serbia.

Paper presented at the 1st International Conference on Accomplishments in Sustainable Development (ICASUS) - Sustainable Development and Biodiversity Conservation, Bosna i Hercegovina – Republika Srpska, Banja Luka, May, 13 and 14, 2011.

Recived: 01.04.2011.
Accepted: 20.06.2011.

Original scientific paper
UDC: 616.8-056.83:316.624

New Regulations and Sustainable Solutions Removal of by-Products of Slaughtered Livestock

Đorđe Okanović[1*], Milutin Ristić[1], Veljko Đukić[2], Šandor Kormanjoš, Vesna Matekalo-Sverak[3], Zvonko Nježić[1]
[1]Institute for Food Technology, University in Novi Sad, Bulevar cara Lazara 1, Novi Sad, Serbia
[2]University Apeiron, Pere Krece 13, Banja Luka, Republic of Srpska
[3]Institute of Meat Hygiene and Technology, Kaćanskog 13, Belgrade, Republic of Serbia

Abstract: The environment is now threatened by the creation and accumulation of waste materials in all branches of industrial production and in the meat industry. The importance of harmless removal of animal waste increases with the intensification of animal breeding and with the development of meat processing plants..

Problem solution of harmless removal of animal origin waste products has the big importance. It is irreplaceable, namely preventive veterinary and sanitary measure used in control of livestock diseases and zoonosis. Nowadays, it has a big role in environment protection.

In the world, the best way of harmless removal of animal waste from meat industry as well as died animals is exactly their collecting and utilization (for feed production, chemical industry and fuel), depending on raw material structure and its characterization, their processing in special plants with modern equipment and technology.

It was emphasized that objects for animal waste processing should be treated from the two aspects: as processing plants serving for the environment protection and as possible environment polluters.

Key word: animal by-products, harmless removal, utilization of by-products, environment

Importance of Safe Disposal of Animal by-Products

Necessity of solution for safe removal of animal by-products by their utilization with processing into animal feed and bioenergents, grows with the intensification of animal growing and the increase of capacities of industrial slaughterhouses, uprise of new small slaughterhouses, building of plants for meat processing and increase of the volume of international trade of commercial animal products [1].

Correct solution for safe disposal of animal by-products can be perceived through three key aspects that should fulfill the technological solutions for solving of disposal of such materials by their processing, namely:

- the epidemiologic-epizoothiologic aspect,
- aspects of environment protection, and
- economic aspect.

a) Epidemiologic-epizoothiologic aspect

Having in mind that animal products (inedible by-products of animal slaughtering, died animals and other waste from cattle-growing farms) must be treated as potential sources of infective diseases of human beings and animals, their sanitary disposal ought to attach an exceptional significance [2].

Ristić et al. [3], in their research articles state that, in breeding stocks of animals, exist the individuals, which, in spite the fact that they do not show any clinical signs of diseases, carry in themselves definite

* Corresponding author, e-mail: djordje.okanovic@fins.uns.ac.rs

pathogens, which they during their life excrete into environment (feces, urine) and after their natural death or slaughtering such carriers can be found in their carcasses or slaughterhouse waste. Many carriers which occur in such waste materials can relatively long keep their viabilities, and after that they can in different ways reach into the environment. For aerobic bacteria survival in tissues of died animals, conditions are better if animal was not buried, especially if the degradation process runs in the environment with optimal moisture content [4].

Exceptionally high dangers represent the animals that died from the infectious diseases, whose carriers are spores, and those are the cases with anthrax and the gas edema. Sporogenous forms are very resistant to the environmental factors, so that their survival life is long-lasting. According to Ristić et al. [5], the number of recognized zoonoses in the World is high (about 180), and we are witnesses of the appearance of some new ones, which until today were not registered as zoonoses (lime-boreliose, Ebola hemorrhagic fever, ehrlichiosis and from the year 2005 officially the bird flu as well).

According to the World Health Organization data, momentous epizoothiologic – epidemiologic situation in the World points to the fact that the high number of communicable diseases shows trends of expansion, so that, with justification, it can be said that mankind's future belongs to the communicable diseases that, day by day, take their tribute on distinct parts of the World. Cited data confirms that animal by-products, from epizoothiologic and epidemiologic point of view, represent high dangers with respect to animal and human health, and this necessitates needs for rapid and efficient, and at the same time, safe disposal of the mentioned materials [6].

b) Aspects of the environment protection

Today, even more and more attention is paid to the protection and upgrading of human environment, because it is threatened by the creation and accumulation of waste materials. The country strives to produce highest possible quantities of material properties that should satisfy human's needs for the best possible standard of living and to create optimal conditions for maintaining of sanitary conditions. Nevertheless, together with welfare properties that are necessary for human being, modern technical civilization creates high quantities of waste, which exert negative effects on the environment, degrading it to such degree that it becomes harmful to the health of people and animals [2].

Polluters are numerous inorganic and organic substances that reach in an organism by contaminated air, water and primarily, food. Their quantities are small, but in the course of time, they accumulate in an individual tissues and organs, causing diseases, degeneration or even death of organisms.

It seems that, together with aspirations for something better, it can have opposite consequences. This is fully applicable on agricultural and cattle growing production, which survived many changes. Such one tendency has been enabled by industrial preparing of feed and with even higher automation and mechanization of cattle growing. Dead animals, and inedible slaughterhouse by-products, as waste materials created in the production process, must be safely disposed, or, otherwise, they can become a serious brake for further development of production, in this case of food, and as such, they are serious polluters of the environment [7].

With the strengthening of production process in cattle growing and production of even higher quantities of meat, the problem of died animals as well as of heaping up of slaughterhouse waste emerges. Dead animals, and inedible slaughterhouse by-products, as waste materials created in the production process, must be safely disposed, or, otherwise, they can become a serious brake for further development of production, in this case of food, and as such, they are serious polluters of the environment. On the other hand, they can so severely contaminate the environment, that it begins to hinder intellectual and operative capabilities of human beings and disables the possibilities for their recreation [8].

Animal waste during putrification contaminates not only the atmosphere, but also the terrain, food and water. The greatest part of blood terminates in the sewage, i.e. in waste water, and only small share of blood is collected and processed [9]. Water courses are physically polluted, and at the same time, in such environments, blood appears as nutrient for microorganisms, many of which are strains, pathogenic for human beings and for the animal kingdom. Biological oxygen demand of blood, according to Baras et al. [10], is about 100,000 mgO_2/L. In the year 1982, contamination of water courses with waste blood in SFR of Yugoslavia was about $57 \cdot 10^9$, which corresponds to the pollution caused by about 1 million of inhabitants.

Pollution of the environment by animal waste shows other adverse effects as well. Such places are also locations with ideal conditions for development of other insects and rodents. They enable the spreading of infections and substantially contribute to the degradation of visual acceptance of environment in which they live. Aesthetic unacceptability of so threatened environment is one of the problems that deserve even more space and time. Disrespecting of the rules on safe disposal of polluters reflects on soil-, atmosphere-, surface- and underground water qualities in the neighborhood, i.e. on climate and, further, on plant- and animal kingdoms and on health of human beings or, definitely on the eco-system as the whole [9].

c) Economic aspect of disposal of dead animals and inedible by-products obtained from slaughtered animals

Economic side of this problem implies collection and safe disposal of huge quantities of biological materials that necessitate costs, which have to be incorporated in prices of the obtained products. If waste of animal origin was not processed (recycled), it represents lost raw material that is possible to incorporate in production of proteinaceous - energetic feed, technical fat for chemical industry, or of fuels with high calorific value [9].

According to the European Union directives included in the Regulation (EC) N^o 1609/09, by the processing of sanitary safe inedible by-products obtained during slaughtering of animals (materials Category 3), it is possible to obtain:

- proteinaceous, protein-mineral and energetic products aimed for animal feeding,
- technical fats,
- feathers for textile industry,
- skins, horns, hoofs, hairs,
- and from died animals (materials Category 2):
- meat-and bone meal as an energent,
- technical fat as an energent or raw material for further processing in chemical industry for production of bio-diesel, and
- biogas, compost.

Safe disposal of the described animal waste (material Category 1) by combustion at high temperatures (over 850°C) enables obtaining of warm water or steam as an energent for processing plant that uses warm water or steam, and ash as construction material for roads.

We shall mention only that, with the respecting procedures of blood collection and its technological processing, various articles for human use can be obtained, primarily products, which are used as functional additives in manufacture of meat products. Special processing procedures enable their use as raw materials in pharmaceutical industry or for production of functional foods [11].

On the other hand, industrial waste blood can be collected and processed using corresponding technological procedure in a plant for processing of other animal by-products, using special processing unit. Such one procedure enables obtaining of feed with high protein content, which, mostly, contains high quantities of essential amino acids, vitamins and mineral substances, and particularly iron [12].

Articles (meat- and bone meal and fat) obtained by processing of materials of Category 1 are suitable for use as energetic fuel, i.e. as fuel for direct combustion in architecturally separated objects, respecting the corresponding legislative rules.

If all cited aspects were treated correctly, it is clear that organized processing and disposal of innocuous inedible slaughterhouse by-products obtained from slaughtered or died animals is of great importance for prevention of spreading of contagious diseases, successful protection and rehabilitation of the environment and for rational usage of such waste.

Classification Categorization and Approximative Quantities of by-Products in the Republic of Srpska

Considering hazards of outspreading of contagious diseases among humans and animals, and possibilities of their total or partial utilization, animal by-products are categorized in three categories. According to the investigation of numerous researchers and the Regulation No. 1069/09 of European Parliament and of EU Council, for animal feed only animal by-products classified as products of Category 3 can be used. Materials of Category [13] 1 must be safely disposed by their combustion in specially constructed furnaces or thermally processed into meat-bone flour and grease. Flour has to be safely disposed by combustion, and grease has to be processed into bio-fuel. Materials classified as Category 2 materials, with respect to the mass occurrence of the described zoocenoses and diseases of animals, can be made safe by one of the processing methods and so obtained protein-mineral part has to be combusted or composted, and the melted fat can be used as raw material for chemical industry [6], [14], [15], [16].

Upon review of the total slaughter of livestock in the Republic of Srpska in 2009 (www.rzs.rs.ba), and the average amount of by-products obtained by slaughtering animals [3], we give the quantities of inedible by-products of slaughtered animals.

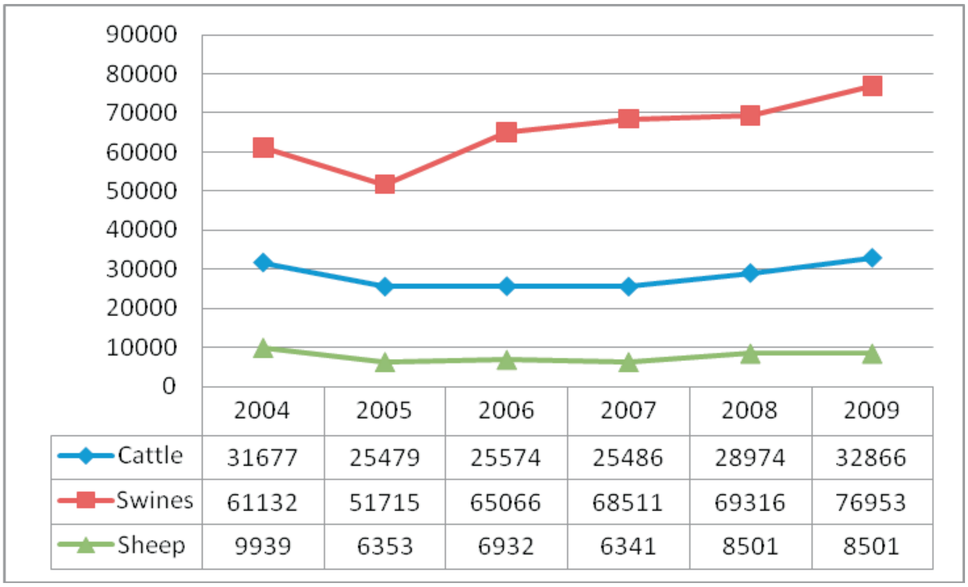
Overview of potential quantities of non-edible by-products from slaughtered animals in the Republic of Srpska are summarized in the Table 1.

Table 1. Animal waste quantities in the Republic of Srpska in 2009 (www.rzs.rs.ba) [17]

Origin of waste	Slaughtered animals, pc	Meat/pc, kg	Meat, t	By-products/pc, kg	By-products, t
Cattle	32 866	175	10 896	44,79	1 472
Swine	76 953	68	6 921	7,18	553
Sheep	8 501	17	290	7,16	61
Poultry	7 545 310	2	15 804	0,60	4 527
TOTAL			33 911		6 613

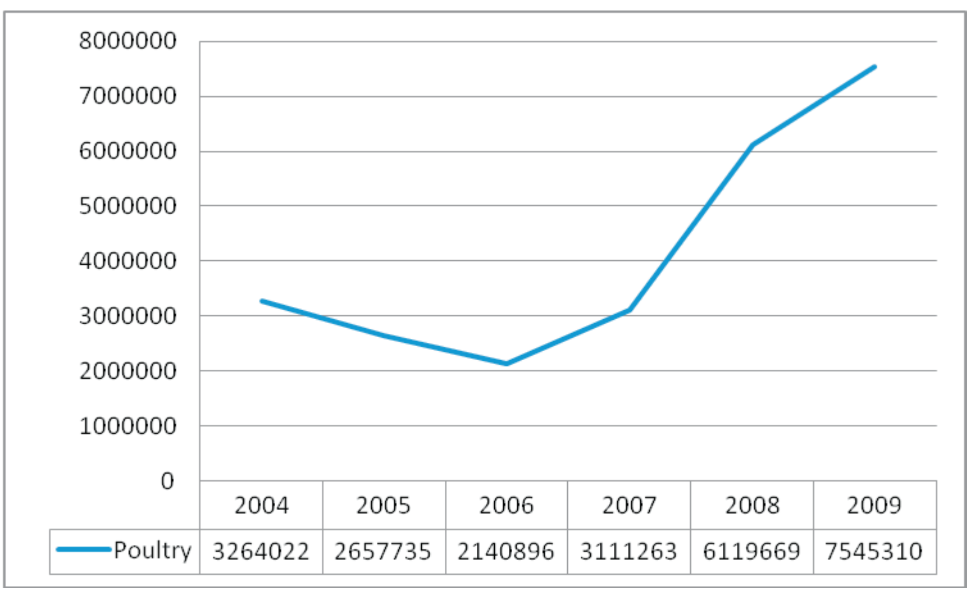
In the Republic of Srpska in 2009, 32,866 cattle were slaughtered, 76,953 pigs, 8,501 sheep and 7,545,310 piece of animals, so as a result we have received 33,911 tons of meat and 6613 tons of animal waste. It is about 22 tons per day, 127 tons per week.

Quantity of animal waste which appears in circulation of goods (raw meat, intestines, cured products, sausages, fat) as well as quantity of died animal corpses which can be collected, should be added to this quantity. If the production of livestock and meat industry is not going to change drasticty, there is 7.000 t of the animal by-products annualy or cca 23.5 t daily, which should be harmlessly removed.



	2004	2005	2006	2007	2008	2009
Cattle	31677	25479	25574	25486	28974	32866
Swines	61132	51715	65066	68511	69316	76953
Sheep	9939	6353	6932	6341	8501	8501

Figure 1. Slaughtered livestock in Republic of Srpska from 2004-2009. (www.rzs.rs.ba) [17]



	2004	2005	2006	2007	2008	2009
Poultry	3264022	2657735	2140896	3111263	6119669	7545310

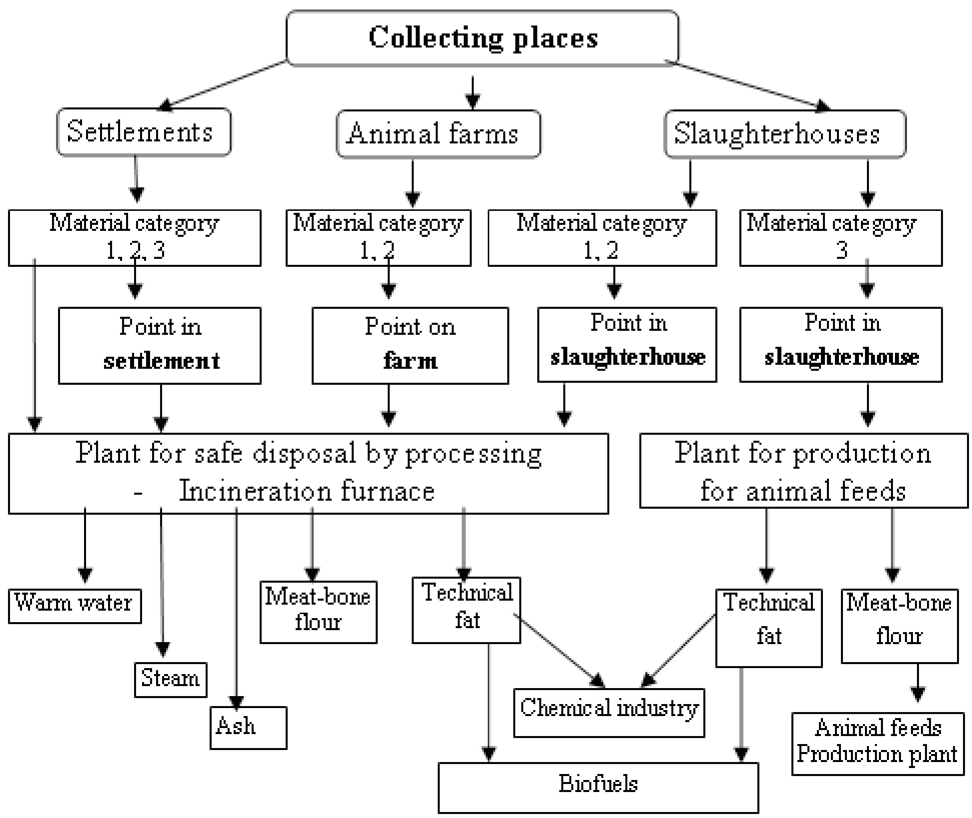
Figure 2. Slaughtered poultry in Republic of Srpska from 2004-2009. (www.rzs.rs.ba) [17]

Based on the number of slaughtered livestock in the Republic of Srpska in the last six years (Fig. 1 and 2) and trend, we can expect an increased number of livestock and thereby slaughterhouse waste. These numbers only indicate the size and significance of the problem.

Organizing of Collection

For proper sanation of animal waste using one of the methods for their safe disposal and fully sanitary hygienic use of non-edible by-products from slaughtered animals, special importance has organized collection, storaging and delivery of raw materials into facilities for their technical processing. Contemporary plant for sanation of this kind of waste represents industrial plant with permanent and regular supplying of raw material. It is extremely important for the safe disposal of animal waste that each object has the correct recognition of its raw materials basis, i.e. formation of the collecting circle that enables obtaining of adequate quantities of animal waste of the given category [18].

Organizing of collection, storaging and transportation of animal waste is shown in Scheme 1.



Scheme 1. Organizing of collection, storaging and safe disposal of animal waste.

In the collection circle organization even the mode of collection of animal by-products is of complex nature, and from solving of which to a great part depends their hygienic and safe disposal and utilization.

Organization of collecting of mentioned raw materials has to be based on connection of objects for non-harmful disposal of dead animals and slaughterhouse waste (slaughterhouses, meat processing plants and animal breeding farms as well as other industries dealing with animal processing). Organization could be composed of a number of corresponding points for storaging of waste within slaughterhouses and meat processing plants, as well as within settlements with larger concentrations of livestock. Point (collecting place) represents a hygienic object aimed for collection and storaging of died animals and of non-edible by--products obtained from slaughtered animals. During the uprising of such points, the initiative of objects for non-harmful disposal should also be implied, gravitating to the establishment of a good organization of collecting, with sanitary service accompannied by qualified sanitary technicians and all necessary equipment for collection and transportation of animal waste classified into mentioned categories [14].

Animal by-products and waste must be identified and labeled with their categories – category 1, 2 or 3 material, at their generation place, so that they remain identified during their collection and transportation. Identified raw material has to be resumed at collecting points into vehicles and transported into storage (point) for storaging of animal by-products and waste separately according to their categories (materials 1, 2 or 3), or directly to processing plants.

Transportation of animal waste

Truck fleet contains special vehicles for resuming of raw materials at points of death, which accomplish transport of materials to the point of collection and from that point to the object of their safe disposal.

Non-edible by-products from great slaughterhouses (classified in categories) are directly transported into reception rooms for their safe disposal.

Vehicles take over the identified raw material on collecting places and transport it in storage (point) for keeping of animal by-products and waste classified in categories (materials 1, 2 and 3) or directly in processing plants [4].

Methods of Sanation of Animal Waste

Each period of economic development and scientific cognition in human and veterinary medicine leaves its contribution in understanding and solving problems of safe disposal of animal waste. Regardless of historical period, basic aim of the activities in this domain was to achieve rapid degradation of organic substances and to inactivate eventually present infective organisms, with, at the same time, prevention of contacts of human beings with the contagious materials.

Changes in the modes of rehabilitation happened with the appearance of neurodegenerative diseases of animals and human beings that characterize spongiform degeneration of brain – diagnosed as spongiform encephalopathy of bovine animals, i.e. the BSE, whose carrier, as it was found in the year 1986, is feed containing inadequately produced meat-and bone meal obtained from ruminants [14], [15].

According to the contemporary regulations in the European Union (Regulative (EC) N° 1069/2009), animal waste can be safely disposed, depending on their category, with the following methods:

1. burying on graveyards for pets,
- burying on locations where organizing of other methods of safe disposal is hardly practicable because of the inaccessibility or for some other reason,
- burying at the place of outbreaks when just described contagious diseases happen,
2. incineration of raw waste in special furnaces at high temperatures (850 – 1200°C),
3. combustion or co-combustion, after technical processing in the plant, which fulfills conditions for such method of safe disposal,
4. processing with production of compost and biogas, and
5. thermal processing into feed.

Prerequisite for safe disposal of animal waste using one of the described methods is organized collection and delivery of raw materials. Modern disposal of waste materials demands orderly constructed plants with adequate capacities, which should assure permanent and continuous supply of raw materials.

Exceptionally important is to emphasize the necessity of transfer of animal waste from the place where it was generated to the storage place as fast as possible, as well as the necessity of rapid performance of the procedure of its processing. This is very significant, not only from the epidemiologic-epizoothiologic aspect or from environment protection aspects, but equally from the aspect of its technical processing. Namely, fresh raw materials are processed easier, with generation of lower quantities of waste gases and obtaining of better quality products [8], [5].

The acceptation of safe disposal of animal waste for its processing and incineration excludes classical forms of disposal (holes, animal graveyards), except for exceptional occasions, so that localities for such objects, nevertheless should be foreseen.

Economic side of this problem implies collection and safe disposal of huge quantities of biological materials that necessitate costs, which have to be incorporated in prices of the obtained products. If waste of animal origin is not processed (recycled), it represents lost raw material that is possible to incorporate in production of proteinaceous - energetic feed, technical fat for chemical industry or of fuels with high calorific value [19].

Acknowledgements

This research was part of the Project No 46009 "Improvement and development of hygienic and technological procedures in producing food animal origin in order to obtain high-quality and safe products competitive on world markets", funded by the Ministry of Science and Technological Development Republic of Serbia

Conclusion

Economic and overall development of the Republic of Srpska will have to increasingly be based on the organized research and development, which should produce permanent technological development as a development of existing and creation of new products, processes and services. The aims can be characterized as a multi-relevant in many aspects:

- Agricultural and food industry by-products, if not valorized, are disposed on landfills, in lagoons, buried in arid terrains or in open water courses, thus contaminating the environment.
- If all mentioned ecological and economical aspects are recognized properly, it becomes clear that organized solving of safe disposal of inedible by-products obtained from slaughtered or died animals by their technical processing is a valuable task.
- To the most rational solutions of their disposal belong their processing into feed, or raw materials for chemical industry and production of bio fuels. By manufacturing feed from sanitary safe raw materials (animal by-products belonging to Category 3 products), they are multiply valorized, with assurance of the rational development of cattle growing and protection of the environment.
- Application of bio fuels contributes to the reduction of oil consumption (i.e. of imports), reduction of emissions of detrimental gases, stimulation of sustainable development of rural regions

- Systematic research, integrated into all the interdependence and condicionality, ensures that aims are achieved not through partial progress in technological development, but for the sustainable solutions that will bring long-term technology development and prosperity.

References:

[1] Okanović Đ., Zekić V., Petrović Ljiljana, Tomović V., Džinić Natalija. (2006): Ekonomičnost proizvodnje svinjskog mesa u polutkama, *Tehnologija mesa*, (XLVII), 5-6, 237-41.

[2] Okanović, Đ., Ristić M, Delić, Stanislava (2008): Sporedni proizvodi poljoprivrede i prehrambene industrije i kvalitet životne sredine, Kvalitet, 65-8.

[3] Ristić M., Okanović Đ., Sakač M. (2011): *Karakteristike životinjskih sporednih proizvoda i njihova namena,* Monografija, FINS Novi Sad, 1-193, ISBN 978-86-7994-013-1.

[4] Ristić M., Okanović Đ., Radusin Tanja (2008): Contemporary approach to animal by-products disposal problems, *Food processing, quality & safety*, 35, 2, 81-92.

[5] Ristić, M., Okanović, Đ., Matekalo-Sverak, V., Kormanjoš, Š. (2008b). Ispitivanje mogućnosti korišćenja creva svinja za proizvodnju proteinskih hraniva, *Tehnologija mesa,* 49, 5-6, 159-201.

[6] Ristić M., Jovanović M., Sakač Marijana (2001): Spongiofor mna ecefalopatija goveda (BSE) i iskorišćavanje nejestivih sporednih proizvoda zaklanih životinja, *Tehnologija mesa*, 42, 3-4, 212.

[7] Okanović, Đ., Mastilović, J., Ristić, M. (2009). Sustainability of food production chain, *Tehnologija mesa*, 50, 1-2, 140-7.

[8] Ristić, M., Filipović, S., Radenković Brana, Sakač Marijana, Kormanjoš, Š., Ćurčić, R. (1997) Waste gases arising in rende plats for animal and fish waste, *Acta Veterinaria*, Beograd, Vol.47 Nº 1, 33-40.

[9] Ristić, M., Okanović, Đ. (2009). Tehnologija neškodljivog uklanjanja sporednih proizvoda klanja životinja, *8. Kongres veterinara Srbije "Veterinarska medicina, život i zdravlje*", Zbornik kratkih sadržaja, 224, Beograd.

[10] Baras J., Turubatović L., Matekalo-Sverak V. 2007. Cleaner production is the pathway to sustainable development. *Tehnologija mesa* 48, (1-2): 83-92.

[11] Matekalo-Sverak, V., Turubatović, L., Babić, J., Trbović, D., Milićević, D. (2007): Utilization of powdered hemoglobin in formed meat products. *Proceedings, 53rd ICoMST*, Beijing, China, 431-2.

[12] Lilić, S., Janković, S., Matekalo-Sverak, V., Turubatović, L., Okanović, Đ., Radičević, T., & Stefanović, S. (2009). Mogućnost korišćenja jetre i bubrega goveda i svinja u ishrani ljudi. *Tehnologija mesa*, 50(5-6), 358-65.

[13] REGULATION (EC) No 1069 (2009). of the European Parliament and of the Council.

[14] Ristić, M., Sakač Marijana, Filipović, S. (2003): Animalni otpaci i njihova sanacija u Srbiji, *Međunarodna eko-konferencija: Zaštita životne sredine gradova i prigradskih naselja*, 397-401, Novi Sad.

[15] Prince M.J., Bailey J.A., Barrowman P.R., Bishop K.J., Campbell G.R., Wood, J.M. (2003): Bovine spongioform encephalophaty, *Rev. Sci Tech. Of int Epiz* 22 1, 37-60.

[16] Kormanjoš Š., Ristić M., Filipović S., Okanović Đ., Radović Vera (2007) Ispitivanje hemijsko-nutritivne vrednosti kaše od perja i njena upotrebna vrednost, *Žito-hleb*, 34, 5-6, 147-51.

[17] www. rzs.rs.ba

[18] Okanović Đ., Ristić M., Nikolić-Stajković S. (2011): Remediation of by-products from slaughtered animals in regard to new regulations, *Tehnologija mesa* 52, 1, 31-8.

[19] Okanović, Đ., Tica, N., Zekić, V., Vukoje, V., Milić, D. (2010). Profitability of investment in plant for processing animal waste, *Technics Technologies Education Management,* 5, 2, 296-300.

Recived: 01.04.2011.
Accepted: 20.06.2011.

Contents

ISSN 1986-6020