

# BIOMASS A REGENERATING SOURCE OF THERMAL ENERGY FOR DRYING INSTALLATIONS

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#### **ABSTRACT:**

I order to reduce  $CO_2$  emissions in accordance also with the principles of durable development, we analyzed the feasibility of using available sources of biomass for supplying thermal energy to installations of agricultural products convective drying. For economical efficiency increasing and optimum development of agricultural products resources which can be kept by drying, the dryers must be placed or displaced as close as possible to the source of products which are to be dried. This aspect limits the fossil, fuels used in Diesel oil and GPL. In this paper we determined the economical and ecological efficiency of supplying thermal energy to a convective dryer. This dryer was realized in CEEX program projected to be capable of using a large fuel variety in conditions of using wood biomass from industrial and forest waste, from maize energetically culture: maize grains and stalks, compared to a Diesel oil using, both for warm water and for drying agent direct warming. At present, from an economical point of view no significant differences are realized, but from an ecological and social point of view the biomass using is to be preferred.

#### **KEYWORDS**:

biomass, agricultural products, economical and ecological efficiency

# **1. INTRODUCTION**

The dehydration is at present one of the principal methods of fruit and vegetables conservation, with a specific reduction of energy expenditure. At industrial level, the dehydration of the food products, characterized by relatively low cost of goods, is used on a large scale because the final products have reduced weight and volume. Thus, by a rigorous control of technological process, is assured the putting into present regulations of hygiene and food security of all food products.

The principal concerns at global level in fruit and vegetables the dehydration in the last 10 years had as objective the drying process and the modalities of its control.

The most significant effects of the automatically controls drying process are: - reduction of specific costs of goods;

- reduction of the number of the operators and associated costs;
- **4** reduction of specific energy expenditure;

Other method used in the last 20 years, in the fruit and vegetables dehydration is the utilization of unconventional sources of energy. On these lines, were realized the drying installations using sun energy, the heat of geothermal waters, the installations of a biogas production, the combustion installations of scraps, thermo-chemical gasification of biomass etc. The convective drying process demands much thermal energy that can be produced from burning agricultural biomass in installations with high efficiency and safety in operation. During the development of agriculture it was indispensable to extent the efficient utilization of available resources and the reduction  $CO_2$  emission.

The convective drying of vegetables and fruit is at present and in perspective, one of the most important modalities of conservation and efficiency of vegetables and fruit.



### 2. DRYING INSTALLATIONS FEEDING WITH THERMAL ENERGY PRODUCED FROM BIOMASS

It is for  $CO_2$  emission reduction and in accordance with the principles of durable development to recommend the using on a large scale of energy regeneration resources that have performances possible comparatively presented in the table 1.

		Table 1		
System	Possible power (kW)	Cost installed power EUR/kW	The energy cost EUR/kWh	Starting up period (years)
CFV (s)	0,5 - 100	10000 - 15000	0,25 - 0,4	0,5
Thermal solar	10 – 30 MW	2 – 3 mil	0,15 - 0,25	3 - 4
Aeolian (s)	200 - 2000	1000 – 5000	0,07 - 0,1	0,5
Micro-hydroelectric plant (s)	20 - 100	1000 - 1500	0,05 - 0,08	1
Biomass	2 - 500	1000 - 1500	0,05 - 0,08	0,5

The specific prices for primary thermal energy and that available obtained from different sources of energy are presented in the table 2.

Table 2									
Combustible type	Calorific power	Specific primary price Lei/kWh	Utilization efficiency (%)	Useful specific price Lei/kWh					
Diesel oil	38,7 MJ/l	0.280	85	0.329					
GPL	26,9 MJ/l	0.295	90	0.328					
Electricity	3,6 MJ/kWh	0.321	100	0.321					
Wood: chips, pellets, chopped	18,5 MJ/kg	0.039	75	0.052					
Corn grains	16,2 MJ/kg	0.100	80	0.125					
Corn stalks	17,5 MJ/kg	0.066	70	0.094					
Switch-grass: pellets	15,2 MJ /kg	0.043	80	0.054					

At present in the biomass market obtained by cultivation in the agricultural lands, corn and switch-grass compressed in pellet have imposed. From comparative energetic analysis of the corn and switch-grass using for the production of alcohol or thermal energy results the data presented in the table 3.

Parameter	UM	Corn for alcohol	Corn for thermal energy	Switch-grass for alcohol	Switch-grass for thermal energy
Annual production	t/ha	6.5	6.5	10.0	10.0
Reaped primary energy	GJ/ha	136.5	136.5	185	185.0
Energy after processing	GJ/ha	64.2	136.5	73.0	175.8
Consumed Energy in processing and conversion	GJ/ha	42.8	2025	15.6	12.7
Net thermal energy	GJ/ha	21.4	115.0	47.2	163.1

Table 3

For thermal energy production from biomass, the following methods can be used: burning in layer, in boilers of hot water; gasification and burning in the same enclosure, in boilers of hot water; gasification in a gas generator and burning in a separate furnace, part of a heat exchanger.

Each method has both advantages and disadvantages and is used in function type of application. For heating air in the convective dryers, whereupon using biomass like combustible, are used heat exchangers of the following type: hot water/air; burned gas/air; vapor/air (seldom).



# 2.1 Examples of the convective dryers with thermal energy from biomass

Forwards are presented typical examples of convective dryers fed with thermal energy produced from biomass.



Fig. 1 The functional diagram of a convective dryer of type USCMER 30/60



Fig. 2 Convective dryer of type USCMER 30/60

In figure 1 is presented the functional diagram of a convective dryer that has a small capacity of USCMER 30/60 type realized inside CEEX PROGRAM. This uses for moisture eliminator heating hot water produced in a reservoir fed with diesel oil or wood biomass.

In figure 2 is presented the convective dryer USCMER 30/60 installed in the drying section.

In the figure 3 is presented the functional diagram of a convective dryer in which the air is fired with a heat exchanger burned gas/air in that to burned the gas of generator produced by a generator gas manually fed in batches, with biomass.





In figure 4 is presented the dryer FD-50 produced in Thailand, with a drying surface of  $15 \text{ m}^2$ , feeding with thermal energy from generator gas of the type cross-draft.



Fig. 4 Dryer FD-50 fed with thermal energy from a cross-draft gas generator

## **3. THE COMPARATIVE ANALYSIS OF FEEDING WITH THERMAL ENERGY FROM BIOMASS**

In order to draw a conclusion concerning the opportunity of biomass using for producing thermal energy utilizable in convective dryers, has been realized a model and a program of simulation for technical-economic analysis of a dryer with the base parameters: drying surface: 30 m<sup>2</sup>; efficient thermal power: 60 kWt.

We have analyzed three variant of feed a moisture eliminator:

1 - heat exchanger hot water/air + boiler of hot water with burning of diesel oil; 2 - heat exchanger hot water/air + boiler of hot water with burning of wood biomass with two stages, gasification + final burning;

3 – heat exchanger burned gas/air + gas burner of generator + gas generator of wood biomass.

In table 4 are presented the principal characteristics of a convective dryer used as a base for the comparative economic analysis.

Size	UM	Value
Drying surface	mp	30.00
Maximum thermal power	kŴt	60.00
Medium efficiency drying fruit	-	0.40
Medium efficiency drying vegetables	-	0.25
Medium specific loading fruit	kg/mp	10.00
Medium specific loading vegetables	kg/mp	8.00
Medium during batch fruit	h	6.00
Medium during batch vegetables	h	10.00
Drying period fruit	months	4.00
Drying period vegetables	months	4.00
Drying period fruit	h	2880.00
Drying period vegetables	h	2880.00
Maxim total function annual hours	h/year	5760.00
Medium loading dryer	-	0.75
Total hours used annual	h/year	4320.00
Diesel oil price	RON/l	3.00
Electric energy price	RON/kWh	0.32
Using biomass price	RON/t	100
Calorific power diesel oil	MJ/kg	42.00
Calorific power wood combination	MJ/kg	15.00
Fresh fruit medium price + transport	RON/kgfp	1.20
Dried fruit selling medium price 15 EUR	RON/kg	51.00
Fresh vegetable medium price + transport	RON/kgfp	0.80
Dried fruit medium price 12 EUR	RON/kg	40.80

Table 4

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Indicator	dicator UM		Hot warm-Diesel oil		Hot water -Biomass		Gas generator - Biomass	
	-	fruit	vegetables	fruit	vegetables	fruit	vegetables	
Production Cost	RON/kg	12,77	17.99	11.06	13.80	11.44	14.00	
Fresh material	%	41,75	26.68	48.25	34.80	47.86	34.40	
Hand-made	%	31.15	33.50	36.00	43.70	37.50	43.05	
Energy	%	17.55	28.84	3.81	6.00	4.50	7.24	
Redeeming and maintenance	%	9.55	10.99	11.95	15.52	11.95	15.41	
Rate	RON	9	4400	102200		103000		
Net annual profit	RON/an	184000	186700	194600	208000	194000	206900	
Profit	First year	1.95	1.98	1.91	2.04	1.89	2.01	
installment	First year		3.93		3.95	3.90		
Annual CO <sub>2</sub> emission	t/year	9,732			0		0	

The analysis results of economical profitableness of using different variants of producing thermal energy for the analyzed dryer are synthesized in table 5. The table 5

It is provide that the profit rate does not differ very much in the three analyzed solutions which still confirm the low interest in extending of using the biomass as source of energy for convective dryers. The difference is given by the emission of  $CO_2$  quantity in atmosphere, about 10 t/an.

When the green certificates are paid, the variants of biomass using will became more efficient. There are no evident economical differences between the two variants of biomass using; the gas generator solution which can use a less exigent combustible and with higher humidity and with higher moisture content could be considered as the optimal one for the near future.

The variants of biomass using are better especially in isolated regions. From this point of view, the energy feeding variants of convective dryers from cogeneration installations fed only with biomass are interesting and feasible technically and economically.

# 4. CONCLUSIONS

The vegetables and fruit convective drying tends to became a method used on a large scale in order to keep fruit and vegetables for a long time, which permits the continuous consuming of vegetal products all over the year.

The fruit and vegetables drying do not need a special training which makes it accessible to a large mass of rural and urban population.

It is proved that better economical results are obtained by using biomass as combustible compared to diesel oil using having as an ecological secondary effect the reduction of  $CO_2$  emission.

The constructive variant of dryer with heat exchanger burned gas/air + furnace of gas generation + wood biomass gas generation, has the same economical performances as the hot water + biomass one, but needs a smaller investment, has a smaller weight and is more easily to move to the place of drying material production.

For assuring an energetically independence feasible from a technical and economical point of view the variants of feeding the convective dryers with energy from cogeneration installations fed only with biomass are to be preferred.

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# ANTIMICROBIAL AND ANTIOXIDANT POTENTIAL OF WASTE PRODUCTS REMAINING AFTER JUICE PRESSING

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#### ABSTRACT

Pomace (skin, seeds and flesh) remaining after juice pressing is rich in anthocyanins and other phenolic phytochemicals and could have potential antimicrobial and antioxidant effects. In our study, aqueous and methanol extracts made from the pomace of six fruits, used widely in juice making (*Fragaria x ananassa, Prunus cerasus, Ribes nigrum, R. rubrum, Rubus idaeus, R. fruticosus*), were tested for antimicrobial activity on Gram-positive and Gram-negative bacteria (*Bacillus cereus, B. subtilis, Campylobacter jejuni, E. coli, Salmonella* Typhimurium *and Serratia marcescens*) and on pathogenic *Candida* species (*C. albicans, C. krusei, C. glabrata, C. parapsilosis, C. pulcherrima,*) by broth dilution assay. Total soluble phenol content was measured by the Folin-Ciocalteu method and antioxidant capacity was determined using DPPH.

*C. jejuni and E. coli* were the most sensitive bacteria especially to the methanol extracts. The growth of *C. albicans, C. krusei* and *C. pulcherrima* was not inhibited by any of the extracts. In general, *Ribes* and *Rubus* species were efficient inhibitors. Phenol content and antioxidant capacity was high in the dark colored pomace (up to 50.4  $\mu$ g gallic acid equivalent/mg dry matter content and 83%, respectively).

**Keywords:** pomace, antimicrobial, antioxidant, phenol

# **1. INTRODUCTION**

Phenolic compounds naturally present in fruits have antioxidant activity and can protect the plant from environmental stress and fungal or bacterial infections. The main classes of polyphenols are phenolic acids, flavonoids including anthocyanins, stilbenes, lignans and complex polymers. Waste products remaining after juice processing (peel, seeds, stems, flesh) are good sources of these ingredients. There is an increasing interest to use pomace for the extraction of natural antioxidants and other value added products [1, 2, 3, 4]. The extracted phenolic compounds of pomace could also have antibacterial and antifungal properties [5, 6]. There is a consumer demand for foodstuffs with minimal or no added synthetic preservatives. Natural antioxidants with antimicrobial activities can be used for enhancing food quality and shelf life. Beside food industry, agriculture and medicine can also have benefits from pomace-derived bioactive compounds as natural antifungal and antibacterial agents.

In the present study, the *in vitro* biological activities of water and methanol extracts of pomace (peels, seeds, flesh) remaining after pressing the juice of six fruits were investigated on food-spoiling and human pathogenic bacteria (*Bacillus cereus, B. subtilis, Campylobacter jejuni, E. coli, Salmonella* Typhimurium *and Serratia marcescens)* and on pathogenic Candida species (*C. albicans, C. krusei, C. glabrata, C. pulcherrima, C. parapsilosis)* by broth dilution method.



## 2. MATERIALS AND METHODS

#### 2.1. Strains and culture conditions

*Bacillus subtilis ssp. subtilis BD170, B. cereus var. mycoides ATCC 9634, Escherichia coli SZMC 0582, Serratia marcescens SZMC 0582,* and a clinical isolate of *Salmonella* ser. Typhimurium were grown on T1 medium (10 g glucose, 4 g beef extract, 4 g peptone, 1 g yeast extract, 1 L water). *Campylobacter jejuni* were cultured on Campylobacter blood-free selective agar medium (CCDA; Charcoal cefoperazone deoxycholate agar, Merck). The yeasts *Candida albicans* ATCC10231, *C. glabrata* CBS 138, *C. krusei* CBS573, *, C. parapsilosis* CBS604, and *C. pulcherrima* CBS 5833 were grown on RPMI1640 medium (Sigma).

#### 2.2. Fruits and extraction methods

Fruits investigated in this study were *Fragaria ananassa* (strawberry), *Prunus cerasus* (sour cherry), *Ribes nigrum* (black currant), *Ribes rubrum* (red currant), *Rubus fruticosus* (blackberry) and *Rubus idaeus* (raspberry). Fresh fruits were purchased on a local market (Szeged). Fruit juices were freshly pressed, and the remaining pomace was dried overnight at 60°C and then grounded to powder. One gram pomace was extracted with 3 x 10 ml of distilled water or methanol. The extracts were evaporated to dryness at 100°C in an oven (water extracts) or at 40 °C in a water bath (methanol extracts). The dry material was dissolved in 4 ml distilled water (water extracts) or 10 % methanol-water solution (methanol extracts), and frozen in 1 ml aliquots at -20°C. One sample from each extract was dried again and weighed for dry matter content calculation. The extracts were diluted in the appropriate media for the tests.

#### 2.3. Determination of antibacterial and antifungal effect by broth dilution method

Absorbance of the bacterial or yeast cultures was measured at 620 nm in the presence of the fivefold diluted extract. In each well, 100  $\mu$ l of diluted and sterile-filtered (0.45  $\mu$ m, Millipore) extract was mixed with 100  $\mu$ l cell suspension (10<sup>5</sup> cells/ml) containing the appropriate medium (final dilution of the tested extract was tenfold). Each test plate contained a positive growth control. The samples were tested in triplicate and the results were recorded after 48 h.

#### 2.4. Determination of total soluble phenol content

Phenol content was measured by the Folin-Ciocalteu method at 725 nm. Calibration was made with gallic acid and results are given as  $\mu g$  gallic acid equivalent/mg dry matter content of the extract.

#### **2.5. Determination of antioxidant capacity**

Antioxidant capacity was measured at 517 nm using DPPH (1,1 diphenyl-2 picrylhydrazyl) and determined using the formula: % capacity= $[(A_{control} - A_{extract})/A_{control}] \times 100$ .

## 3. RESULTS AND DISCUSSION

# 3.1. Antibacterial and antifungal effect

Best results were obtained with the dark coloured pomace of *Ribes nigrum* and *Rubus fruticosus*. Both aqueous and methanol extracts of these fruits reduced the growth of almost all bacteria in this study, and *S*. Typhimurium growth was completely inhibited by *R. nigrum* pomace extracts. In general, methanol extracts had stronger inhibitory effect than water extracts. The most insensitive bacterium was the Gram-negative *S. marcescens*, and the most sensitive one, the also Gram-negative *C. jejuni* which was inhibited by all of the investigated extracts (Table 1).

The components present in aqueous and alcoholic extracts are partly dissimilar. Water extract contains the majority of anthocyanins, tannins, starches, saponins, polypeptides and lectins of the pomace, while methanol extracts, in addition, polyphenols, lactones, flavones, and phenons [7]. Phenolic and organic acids acidify the cytoplasm of microorganisms, while certain small hydrophobic molecules, called permeabilisers, can disintegrate the outer membrane of Gram-negative bacteria causing bactericidal effects. Puupponen-Pimia and co-workers [8] found that raspberry extracts caused permeabilisation of *Salmonella* membrane.



	Table 1 Growth infibition effect of pomace extracts on bacteria											
	Gran	n positi	ive bac	teria		Gram negative bacteria						
	B. su	btilis	В. се	ereus	Е.	coli	S. mar	cescens	S. Typhi	-murium	C. je	ejuni
	W	Μ	W	Μ	W	Μ	W	Μ	W	Μ	W	M
Fragaria ananassa	4	1	4	1	4	3	4	4	n.d	n.d	n.d	n.d
Prunus cerasus	4	4	2	4	3	1	4	1	2	0	1	1
Ribes nigrum	1	1	4	0	1	1	1	4	0	0	0	2
Ribes rubrum	4	4	4	4	4	1	4	1	1	1	1	1
Rubus fruticosus	1	1	1	0	4	1	4	2	3	2	1	0
Rubus idaeus	4	4	3	4	4	2	4	1	4	2	1	0

We hypothesized that the presence of such permeabilisers found in methanol extracts can cause the better growth inhibition effect of these extracts.

0 - no growth; 1 - growth<25 %; 2 - growth<50 %; 3 - growth<75%; 4 - growth>75%. Control growth is taken as 100%. W: water extracts; M: methanol extracts. n.d. - no data.

*Candida* species showed lower sensitivity to the pomace extracts. The growth of *C. albicans, C. krusei* and *C. pulcherrima* was not inhibited by any of the extracts. *R. nigrum* and *R. fruticosus* water extracts reduced the growth of *C. glabrata*, and inhibited totally the growth of *C. parapsilosis. F. ananassa* and *R. idaeus* had inhibitory effect on both sensitive Candida species while *P. cerasus* and *R. rubrum* had no effect on any of the yeasts (Table 2).

Similar data on the non-sensitivity of *C. albicans* to plant extracts can be found in the literature [9, 10]. Our results with *C. parapsilosis* were, however, in contrast to those where this and seven other yeast species showed resistance to berry water extracts and juices [11]. Table 2 Growth inhibition effect of pomace extracts on Candida species

	2 010 0		JILIOII	enect	or poin	Iace ent		Janulua S	pecies.	
	C. all	bicans	C. ki	rusei	C. gla	brata	C. pulci	herrima	C. para	psilosis
	W	Μ	W	Μ	Ŵ	Μ	W	Μ	W	Μ
Fragaria ananassa	4	4	4	4	2	4	4	4	1	4
Prunus cerasus	4	4	4	4	4	4	4	4	4	4
Ribes nigrum	4	4	4	4	1	4	4	4	0	1
Ribes rubrum	4	4	4	4	4	4	4	4	4	4
Rubus fruticosus	4	4	4	4	2	4	4	4	0	4
Rubus idaeus	4	4	4	4	1	4	4	4	2	4
	. 1	.1			. 1	0.4		.1		1 01

0 - no growth; 1 growth<25 %; 2 - growth<50 %; 3 - growth<75%; 4 - growth>75%. Control growth is taken as 100%. W: water extracts; M: methanol extracts

#### 3.2. Phenol content and antioxidant capacity

Phenol content of the water and methanol extracts can be seen in Table 3. *R. nigrum* had the highest and *F. ananassa* the lowest value. Antioxidant capacity ranged from 66 % (*R. rubrum*) to 83 % (*R. nigrum*) (Fig.1). It seems that there is no firm correlation between the soluble phenol content and antioxidant capacity. In spite of this, higher phenol content resulted in better inhibitory effect against sensitive bacteria and yeasts. Linear regression between phenol content and antibacterial effect showed R<sup>2</sup> value of 0.6197 for water extracts and 0.5438 for methanol extracts.

Table 3 Soluble phenol content of pomace given as  $\mu g$  gallic acid equivalent/mg

	dry matter content of extracts	
	Water extract	Methanol extract
Fragaria ananassa	$13.61\pm0.17$	$17.0\pm0.33$
Prunus cerasus	$31.43 \pm 0.35$	$\textbf{27.22} \pm \textbf{1.16}$
Ribes nigrum	$49.70\pm0.10$	$50,44 \pm 0.06$
Ribes rubrum	$28.16 \pm 0.13$	$\textbf{20.54} \pm \textbf{0.66}$
Rubus fruticosus	$23.88 \pm 0.61$	$46.50 \pm 2.50$
Rubus idaeus	$29.71\pm0.71$	$36.72\pm3.70$

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Fig. 1 Antioxidant capacity of fruits pomace extracts

Pomace remaining after juice processing is not a waste product. It is rich in extractable bioactive compounds, and can be used in various ways in the food industry as source of natural antioxidants and/or preservatives. There is also a perspective to use the antimicrobial capacity of pomace in agriculture and medicine. Our results suggest that especially dark coloured pomace, extracted with solvents for hydrophobic molecules, are good candidates as antimicrobial agents.

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# MAPPING OF RISKS ON THE MAIN ROAD NETWORK OF SERBIA

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#### Abstract:

Evaluation of traffic safety is very complex work. During this process it is necessary to define parameters which will represent on the best way risk in traffic.

In the paper are presented methodology of work and most important results from study "ROAD ASSESSMENT PROGRAM ON THE MAIN ROAD IN SERBIA". Investigation is taken for period of five year (2002.-2006.) with special consideration on analyze of traffic safety on the main road. We pay attention on the great significance of road assessment on traffic safety management in Serbia how we advance level of traffic safety and find out micro location with increase risk in traffic on the main road in Serbia.

Key Words: Traffic Accident, Road, Road Assessment, Risk

# **1. INTRODUCTION**

The road network takes a very high position in the hierarchy of significance of impact on traffic safety. Therefore, it is the obligation of the state (as the road manager) to monitor and manage traffic safety of road network through its own mechanisms (organisation, human and technical resources, methodology of work, finances etc.) within its responsibilities. "Risk mapping" is a suitable technique for identification, control, and management of risks on roads.

Risk mapping has been carried out based on the collected, systematised, and analysed quality data on traffic accidents and their consequences along road directions would make a quality basis for all further managing activities aimed at improvement of traffic safety.

It should be pointed out that such risk mapping is carried out for the first time in Serbia and that the best risk mapping practice in the world has been observed (in particular risk mapping in Europe – EuroMAP, risk mapping in Australia - AusMAP, risk mapping in America – usRAP)[2].

# 1.1. The research subject and objective

The subject of the research is the spatial analysis of traffic accidents on the main roads in the territory of municipalities in the Republic of Serbia based on the number of traffic accidents, casualties, and traffic load (AADT – average annual daily traffic).

The main objective of the paper is to calculate the collective and individual risk that was the basis for graphic presentation per sections on the 1<sup>st</sup> rank public roads based on the data on roads, traffic, accidents and their consequences, all aimed at simulating local communities, municipal administrations to do everything that is in their power, as decision makers in the territories they manage, and contribute to reduction of casualties in traffic accidents.

# **1.2. Research period and territory**

The research encompasses the period of five years, i.e. the period from the year 2002 to 2006. The territory includes the first rank public roads in the territory of the Republic of Serbia. The research included 34 main roads in the total length of 4,912.5 km. Those road directions were divided into 558 micro-sections that are homogenous in the sense of road characteristics and traffic.



# 1.3. Limitations in the paper

The limitations refer to comprehensiveness because the research did not include the territory of Kosovo and Metohija. In addition to that, the Analysis is based on available data from the UIS (unified information system) of the Ministry of Internal Affairs (MIA) of the Republic of Serbia, namely, on other public databases so that the quality and access to data determine largely the quality of the research results.

# 2. METHOD OF WORK

The following methods were used in the research of mapping of risks in traffic on the first rank public roads in Serbia:

- Method of analysis (research based on explanation of the problem through dividing of complex thoughts onto simpler integral parts)
- Synthesis (reversed procedure in comparison to analysis);
- Classification method (finding of sets with similar properties);
- Method of comparison (comparison of the same or similar facts, phenomena or processes, namely finding of their similarities in behaviour and differences);
- Statistical method (finding of structures and rules of occurrence within certain intervals based on indicators).

# **3. THE OUTLINE OF THE MOST SIGNIFICANT RESEARCH RESULTS**

## 3.1. Structure of the first rank public roads in the territory of Serbia

Republic of Serbia is one of the European countries with a medium population density and well developed network of the first rank public roads (hereinafter we will use the term "main roads"). Geographical position of Serbia is favourable. A larger number of international roads pass through Serbia, which increases additionally the traffic scope and affects the traffic safety characteristics.

The research encompassed 34 main road directions in the total length of 4,912.5 km. Those road directions were divided into 558 micro-sections – traffic sections that are not homogenous in the sense of road and traffic properties.

The length of roads differs significantly. The longest road is the M-1 road (a branch of the Corridor X through Serbia) with the total length of 494.5 km (10.1%). It is followed by M-22 road that is 487.9 km (9.9%) long and M-24 that is 475.7 km (9.7%) long. The shortest road is the M-14.1 road (2.2 km) (Graph 1).





## 3.2. Analysis of traffic accidents per main roads in Serbia

According to the number of traffic accidents on the main roads in Serbia, we can single out three road directions: M-1 where 9,205 (25.4%) of accidents happened during the analysed period, M-22 with 6,411 (17.7%) and M-5 with 4,176 (11.5%). Almost **55%** of all traffic accidents that happened on the main roads in Serbia happened on the above-mentioned three roads (Graph 2). There were 3,034 (8.4%) traffic accidents on M-21 road.



Graph 2. The number of registered traffic accidents with material damage and casualties, per main roads, Serbia, the period from 2002 to 2006

#### **3.3.** Consequences of traffic accidents

The above-mentioned three main roads in Serbia can also be singled out according to the number of casualties: M-1 with 2,690 (17.7%) casualties within the analysed period, M-22 with 2,383 (15.7%) and M-5 with 1,806 (11.9%) of casualties, along with the road M-21 with 1,432 (9.4%) of casualties (Graph 3). On those four roads, there was 54.8% of the total number of casualties on the main roads in Serbia.

The distribution of the number of casualties of all categories (killed, seriously and less seriously injured) is similar to the distribution of number of accidents with casualties per roads. The number of people who were killed in accidents and number of those who were injured is particularly high on the M-1 road (308 killed, namely 22.5% and 2,382 injured, or 17.3%), M-22 (253 killed, namely 18.5% and 2,130 injured, or 15.4%) and M-5 (136 killed, namely 9.9% and 1,670 injured, or 12.1%) in comparison to all other roads (Graph 3).



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# 3.4. Spatial distribution of risks per roads and traffic safety evaluation

Traffic safety evaluation is an exceptionally complex procedure. During that process, it is necessary to define parameters, which will represent the level of threats in traffic in the proper way and define their quantitative values that are meritory for comparison of results of the set parameters.

The following, generally accepted indices in experts circles were used in the process of identification of dangerous sections:

## **4** Individual Risk of the Killed and Seriously Injured

Setting of the relationship between the number of the killed and seriously injured people in traffic accidents and the number of vehicle kilometres establishes the value of the Individual Risk of the Killed and Seriously Injured.

## Collective Risk of killed and seriously injuried

Collective risk represents relation number of killed and serious injuries in traffic accident and section length. This parameter is representative for ranking micro location according risk in traffic.

After defining of evaluation parameters, it was necessary to commence with their calculation. Based on the data on traffic accidents and their consequences (UIS MIA), each traffic accident and its consequences were "lowered" onto the appropriate road, onto the road section and onto one-kilometre section (kilometre of a road). Individual risks of occurrence of traffic accidents and risks of casualties were calculated for all road and one-kilometre sections of the main roads network.

In such a way, the lowest and highest risk values and risk scope were defined, based on which the following risk classes were adopted:

- Risk scope for Individual Risk is 8 (Table 1), number of the killed and seriously injured on 100 mil. vehic.-km,
- **4** Risk scope for Collective risk of killed and serious injuries is 15 (Table 2)

The risk maps per roads for each micro-section were prepared for all the parameters.

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Ordinal No (mark of	Level of risk	Individua Killed and S Injured for	ll Risk Seriously section					
traffic safety)	(description)	class (interval)	rang (color)					
1	low risk	up to 8						
2	low-medium risk	[8 – 16)						
3	medium risk	[16 – 24)						
4	high-medium risk	[24 - 32)						
5	high risk	over 32						

Table 1. Number of the killed and seriously injured on 100 mil. vehic.-km,

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Table 2	('ollective	Rick	of killed	and	semons	10111	ries
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Ordinal No (mark of	Level of risk	Collective Killed and S Injured for	e Risk eriously section
traffic safety)	(ucseription)	class (interval)	rang (color)
1	low risk	up to 15	(0001)
2	low-medium risk	[15 - 30]	
3	medium risk	[30 - 45]	
4	high-medium risk	[45 - 60)	
5	high risk	over 60	

The risk map shows 30 of the most threatened sections on the main roads network of the Republic of Serbia according to the values of those two evaluation parameters.



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#### 4. FINAL CONSIDERATIONS WITH GENERAL PROPOSAL OF MEASURES

The basis of each activity of traffic safety increasing, namely preventing of traffic accidents and their consequences has to rely on precisely diagnosticised status and clearly defined conditions within which those phenomena occur. The detailed analysis and permanent monitoring of distribution (spatial, temporal) of traffic accidents, namely casualties, enables more efficient planning and implementation of measures and activities aimed at their prevention because the results of such analyses point us when and where we should undertake certain measures.

Risk mapping is one of the most significant techniques in realisation of the abovementioned process. The efficiency of such approach has been recognised in many countries, which achieve the best results in prevention of traffic accidents and their consequences. Risk maps enable simple identification of the safest and most dangerous road sections within a region or a country while the comparison of maps from several countries enables the comparison of safety of the same ranked roads between them.

In the conditions that are currently valid in our country, it is necessary to prepare the data records on traffic accidents in a better quality way so that the accuracy and reliability of data would be at a high level.

At an annual level, it is necessary to carry out the analyses of spatial distribution of risks on the national road network and risk maps should be the output result of such analyses. Such an approach enables defining of priorities in work in the forthcoming period but it also creates the conditions for evaluation of efficiency of everything that has been done within the previous period in the field of improvement of traffic safety on certain roads.

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# UTILIZATION OF WASTE MATERIALS FROM BIOMASS AS ENERGY-GENERATED PRODUCT IN TECHNOLOGICAL PROCESS

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#### **ABSTRACT:**

Climate changes, energy dependency and reduction of fossil fuels lead to great public interest and utilization for renewable energy sources (RES). Demand for renewable energy is consequence of global energy crisis and fact that utilization of solar energy, geothermal energy, eol energy and energy of biomass reduces pollution to environment.

EU and USA are intersted in overall energetic balance, energetic efficience of thermal plants powered by biomass, rationalization of standard fuel dissipation in agriculture and higher level of environmental protection

These paper analyzes possibility for utilization of waste materials from fabricated fruit as energygenerated product for producing heat in technological process.

Key words:

renewable energy sources, biomass, energy efficiency.

# **1. INTRODUCTION**

Consequences of climate changes, energy dependency and reduction of fossil fuels lead to great public interest and utilization of renewable energy sources (RES). Serious interest for renewable energy is the consequence of global energy crisis, but also fact that with usage of Solar energy, wind energy, geothermal water and biomass energy, nature and environment are far more less contaminated. Energy crisis that was engendered at the begining of 2009. when the conflict between Russia and Ukrain started, lead to energy crisis in the most parts of Europe.

# 2. RENEWABLE ENERGY SOURCES (RES)

Renewable Energy Sources (RES), are offering great potencial for future energy consuption, but costs for energy production at these moment are to high.

Therefore it must elapse some period of time before it reaches new dimension of RES appliance. Unfortunately at these moment, human kind must rely on nonrenewable energy sources – oil, coal, nuclear energy and natural gas. RES without hydroenergy, provides about 1% of total energy at these moment. In the environmental approach, future rate must be significantly enlarged, because nonrenewable energy sources are decreasing every day. Development and appliance of RES (especially wind energy, Solar energy and biomass energy) are very important in many different ways. RES have very important role for decreasing  $CO_2$  emissions in atmosphere. With increasing usage of RES, energetic system sustainability is geting more progressive and dependency from importing energy resources and electric power reduces [4].

Towards data that are shareware to public and national statistical database, oil consuption in the world amounts about four billions of tons per year, while on the another hand total oil reserves amounts about 120 - 160 billion tonnes. Oil refinement will achieve peak by 2010. year, and there is the fact that fossil and nuclear fuels offer only short time and nonrenewable development. Fossil fuel reserves are desappearing very fast, in this way many peple predicts two decades before everyone must use RES.

Members of EU have been decided to increase share of RES from 8.5 % in 2005. to 20% by 2020.



EU actions in field of RES lead to higher number of employed people, more than 350.000, and annual transactions are estimated to 30 billions €. World energy consumption by data for year 2000. (TPES – Total Primary Energy Supply) by RES is about 13.5. %.



Figure 1. RES share in world electric power production

The largest share of RES (11%) have biomass and municipal waste, water bodies have 2.3%, while all other RES have 0.5%. For world electricity production in year 2000.,share of RES is about 19% (Figure 1.). Most important share of RES has hydroelectric power plant with 17.48%, biomass and municipial waste have share of 0.95% and all others have 0.57%.

Implementation strategy and RES utilization program with us, such as in all other regions of the world depends from each source characteristics. All other countries have the same target, increasing RES share within energy obtaining in future decades. RES are very important for  $CO_2$  emission reduction. Using of RES significantly bring safe obtaining, first of all

electric power, because it reduces dependency growth from importing energy. RES are separated to:

Classic RES:

- Combustible renewable waste (solid biomass, woodcoal, agricultural and animal waste, municipal and industrial waste, biogas) and
- Hydroelectric power plants.

New RES:

- **4** Small hydroelectric power plants,
- 🖌 Geothermal energy,
- 👃 Solar energy,
- 🖶 Wind,
- Energy of see (sea, tide and low tide, thermal gradient).
- But in wider sense RES means:
- Water power energy,
- Solar energy,
- Wind energy,
- Geothermal enegy,
- Oceans and see energy,
- BIOMASS energy.

# 3. BIOMASS AND WASTE BIOMASS (WBM)

Biomass is organic matter from animal or herbal origin, which converts in many different ways to useful energy.

Energy from herbs represents acumulated solar energy wherewith light is transforming to chemical energy.

Biomass constitute from agriculture waste 98%, forest production 1,5% and wood refining production 0,5%.On the another side biomass can divide to energetic plants, agricultural scrap and waste. Biomass waste from agricultural production is one of the most perspective energy sources in Serbia and beside that biomass do not generate hazardous substances. Seizing of biomass from waste as a fuel can save considerable funds which strive in purchasing of all other energy-generating products.

Biomass and waste materials are utilizing as energy sources for their combustion and heat generation which propel electric generators or for fluid heating. Energy acumulated in biomass is chemical nature so in energy exploatation, there is no work [1].

Biomass energetic potencial is enormous and it amounts about 80% of total RES potencial. That is the energy which is equivalent to 2,6 millions of tons of combusted oil. Technological advance lead to development in technologies which are based on biomass waste, energy and resources that agroindustrial complex unload, but also and all other areas of agricultural development. In the same time, introducing with new technologies shows pozitive impacts on the environment, apropos to environmental protection and improvement. Available biomass in Serbia could be energetic source for unrenewable liquid and gas fuels replacement, so as for electric energy in agroindustrial complex[7].



# 4. "VINO ŽUPA" EXAMPLE

Energy-generating products that are using at the moment in the fabric complex ""VINO ŽUPA' - DD" are heavy fuel oil – mazut and electric energy. Because of constant fossil fuel price changes and obtaining instability, usage of biomass as energy-generating product is reasonable in economic and ecological aspect.

Biomass from waste (WBM), which emergent in agricultural products treatment in fabric "Vino Župa"-Aleksandrovac, management plans to use as motor fuel for biomass boiler which is in instalation phase.

WBM in the case of "Vino Župa" (seeds, stems, apple and grape rapes and wood waste), belong to RES and CO<sub>2</sub> neutral energy sources.

As a fuel in biomass boiler, waste materials from fruits and vegetables production are estimated:

Name	H- humidity [%]	Quantity	Period
Wood waste and sawdust	40	20 m³/day	from 01.06 31.10.
Cherry seeds with foreskin	49	1000 t	from 01.06 30.06.
Cherry, plum, peach, apricot seeds with foreskin	49	1000 t	from 01.07 31.07.
Cherry, plum, peach, apricot seeds with foreskin	49	500 t	from 01.08 31.08.
Apple slurry	84,61	10000 t	from 01.08 31.10.
Grape rape	50,20	2500 t	from 10.09 20.10.
Grape stem	60	2500 t	from 10.09 20.10.

Table 1. Estimated fruit and vegetable production

#### Table 2.Boiler technical characteristics

Туре	SURI P -12/SURI-RGF 15
Production max.	12000 kg/h
Boiler capacity	7812 <i>kW</i>
Max. Preasure	13 bar
Tested preasure	16.9 <i>bar</i>
Max. steam temperature	195 $^{\circ}\!C$
Feeder water temp.	$105^{\circ}C$
Fuel	Biomasa
Lower fuel heat potencial	0008 22 k I/kg
(W=40%, A=0.5%)	9900.22 KJ/ Kg
Boiler efficiency rate	82.57%
Exit flue gases temperature	161 <i>°C</i>
Boiler mass – net	47831 kg
Boiler mass – fatigue	73756 kg
Heating area	900 <i>m</i> <sup>2</sup>
Preasure fall on the gas phase	1600 <i>Pa</i>
Preasure fall on the water phase	0,1 bar
Fuel consumption	kg/h 3437
Air flow	15880 m <sup>3</sup> /h
Flue gases flow on t <sub>exit</sub>	36150 m³/h

Towards data from study of Innovation Centre of Technical Faculty in Belgrade, accessible quantities of biomass are totally appeasing requirements for technological dry saturated steam production with 12 t/h and 12 bar.

Table 3. Average biomass heat potencial							
Biomass	kJ/kg	9908					

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## **5. CONCLUSIONS**

So far "Vino Župa" was utilized mazut as a fuel which leaded to creation of gases that polluted air and environment and contributed to Greenhouse effects.

Since fuel price varied in last couple of years, boiler with biomass satisfied both ecological and environment aspects. Economical calculations pont that boiler will be redeemed for couple of years with current prices of oil and production trend.

That confirms conclusion that biomass is economically payable, but only in cases when biomass was generated in big volumes next to direct exploitation presence.

With examination of analysis we can conclude that there is a strong connection between Strenghts and Opportunities for maximum RES utilization as energy-generating product. But also it is essential to benefit from Strenghts and Opportunities so we could eliminate Weaknesses and Threats.

Corresponding to global trend and requirement for energy, RES has future in resolving ecological and economic world crisis[3].

Strenghts	Weaknesses
<ul> <li>Low-cost resouces – low redemption price</li> <li>Non load waste to environment</li> <li>Good expet sense</li> <li>Good liquidity and profitability</li> <li>Developed technology</li> <li>Production Innovation</li> <li>Biomass is CO<sub>2</sub> neutral fuel</li> <li>Accessibly</li> <li>"Clean" ash</li> <li>High total energy potencial</li> <li>Employing</li> </ul>	<ul> <li>Low fuel power</li> <li>Transport</li> <li>High humidity rate</li> <li>Low energy value by mass unit</li> <li>Different admixtures (Chlor)</li> <li>unhomogeneity</li> </ul>
Opportunities	Threats
<ul> <li>EU access</li> <li>EU strategy for RES – until 2020.year 20%</li> <li>World trends</li> <li>Energy crisis</li> <li>20 boiler producers in Serbia</li> <li>Lower dependency from import</li> <li>Equall and renewable country development, regions development in Serbia and dedication of local communities</li> <li>Agricultural development</li> <li>Cogeneration and threegeneration</li> </ul>	<ul> <li>↓ Law regulations</li> <li>↓ Undeveloped public sense</li> <li>↓ Unfriendly political an economic situation</li> </ul>

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# THREATS IN TRAFFIC FOR THE YOUNG PEOPLE IN THE TERRITORY OF SERBIA

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#### Abstract:

Every year 1.2 million people from all over the world are killed in traffic accidents. Hundreds of thousands of people get injured on the roads, and a very large number of them remain permanently handicapped and disabled for further independent life. The participation of young drivers in traffic accidents with the killed and traffic accidents with injured persons is very high. Injuries in traffic accidents take the second place as causes of death among young people aged 5 to 25.

The paper analyses the characteristics of casualties in traffic belonging to the age group from 15 to 24 in the territory of the Republic of Serbia in the period from the year 2002 to 2006. A special emphasis in the paper is placed on spatial distribution of casualty risk among young participants in traffic. For that purpose, we prepared the public risk map for death in the age groups from 15 to 19 and 20 to 24 per municipalities in the Republic of Serbia.

The objective is to establish spatial distribution of casualty risk for members of those age groups per municipalities in Serbia and to identify in such a way the areas with the highest public risk in traffic.

**Key words:** Traffic, Safety, Risk, Young People

# **1. INTRODUCTION**

Every year, according to the statistics, 1.2 million people are known to die in road accidents worldwide. Millions of others sustain injuries, with some suffering permanent disabilities [4].

The analyses of traffic accidents and their consequences all over the world show a large share of the young people in the number of casualties in traffic. A high level of participation of the young people in traffic accidents is a critical element of social and economic cost for the social community.

Different age groups are characterised by different knowledge, attitudes, capacities, behaviour, and different traffic exposure. Injuries in traffic accidents take the second place as causes of death among young people aged 5 to 25 while among young participants in traffic aged up to 25 young men make 75% of casualties.

Most often, young people show the appropriate physical preconditions but they still lack life and traffic experience, maturity in traffic, which could give the most favourable shape to those preconditions that is necessary for accomplishment of the final aim. They have good perceptive and reaction capacities but that is not sufficient for safe vehicle driving. Among young people, there is often a disharmony between self-confidence, actual psycho-physical capacities of their bodies and technical potentials of their vehicles. In all age groups, overestimating of one's own subjective potentials is a frequent case caused by still undefined self-awareness, insufficiently developed self-consciousness, and self-criticism, unawareness of one's own limitations.

The subject of this paper are the casualties in traffic belonging to the age group from 15 to 24 in the territory of the Republic of Serbia in the period from the year 2002 to 2006. The main objective of this paper is to establish spatial distribution of casualty risk for members of those age groups per municipalities in Serbia and to identify in such a way the areas with the highest public risk in traffic.



There are certain limitations in the paper due to the current social-political situation at Kosovo and Metohija so that this Province has not been included in the research. We used the databases from the UIS (unified information system) of the Ministry of Internal Affairs (MIA) of the Republic of Serbia, so that the quality of results obtained through the analyses depends on accuracy of the input data.

# 2. METHOD OF WORK

In the research of threats to young participants in traffic, we applied the following methods in order to obtain the best quality results:

- 4 Statistical method
- Analytical method
- Classification method (finding of sets with similar properties);
- Method of comparison (comparison of the same or similar facts, phenomena or processes, namely finding of their similarities in behaviour and differences);
- **4** Method of presentation of results in graphs.

Fro the needs of the research we established the database on casualties among young participants in traffic accidents in "MICROSOFT ACCES" programme software. For data processing we used "MICROSOFT EXCEL" programme software, an data were presented on maps for he purpose of easier spotting of municipalities in which it is necessary to implement the traffic safety strategy aimed at reduction of number of casualties among young participants in traffic.

# **3. THE OUTLINE OF THE MOST SIGNIFICANT RESEARCH RESULTS**

# 3.1. Population structure in Serbia

According to the results of the research of the World Health Organisation (WHO) 3,242 persons die on the average a day on the roads in the world. From 20 to 50 million people a year get injured or permanently disabled in traffic accidents. In Serbia, 4,423 persons were killed in traffic accidents in the period from 2002 to 2006 and 83,563 of them were injured. The number of the killed persons aged from 15 to 24 is 625 (15% of the total number of those who were killed) while 21,560 of them were injured (25% of the total number of those who were injured).

In order to be able to analyse and evaluate traffic safety in a country it is necessary, first of all, to analyse the structure (the age structure in particular) of the population of the relevant country.

The last census was conducted in Serbia in 2002 by the Republic Institute for Statistics of Serbia. Persons aged from 15 to 24 make 13.49% of the population (Graph 1).



Age group

Graph 1. Population structure per age groups, Serbia, the results of the census from 2002 [2]



# 3.2. Structure of casualties among participants in traffic according to consequences

The highest share in the structure of casualties among participants in traffic belongs to persons in the age group from 15 to 24 (Table 1). Out of 87,986 of casualties in total in the analysed period 22,185 (25.21%) of casualties belong to the age group from 15 to 24. The number of casualties among members of the age group from 45 to 64 is also very high - 20,212 (22.97%) of casualties among participants in traffic. They are followed by the age group from 25 to 34 and from 35 to 44. If we take into account the fact that the age group from 45 to 64 is far more numerous than the age group from 15 to 24, it is clear that the number of casualties in a younger age group is even more emphasised.

Age group	Killed	serious injuries	light injuries	Number of casualties		
0-9	123	978	3400	4501		
10-14	69	947	2719	3735		
15-24	625	4740	16820	22185		
25-34	642	3736	11429	15807		
35-44	529	2949	7989	11467		
45-64	1320	6010	12882	20212		
65 and elder	1100	3492	5241	9833		
unknow	15	51	180	246		
Sum	4423	22903	60660	87986		

Table 1. Structure of casualties among participants in traffic according to<br/>consequences per age groups, Serbia, 2002-2006



Age group Graph 2. Factor of risk per age group, Serbia, 2002-2006







## 3.3. Spatial distribution of casualties among young participants in traffic

Establishing of the level of threats to certain groups of participants in traffic is most often based on the scope of public risk (casualties and number of those who were killed).

Public risk of deaths in traffic represents the number of the killed young participants in traffic per 100.000 of young people, and number of casualties among young participants in traffic per 100.000 of young people represents the public risk of casualties in traffic.

For the needs of those analyses, we used the following two databases in this paper:

- **4** Number of inhabitants per municipalities in the territory of Serbia
- Number and characteristics of traffic accidents and their consequences per municipalities in the territory of Serbia.

Ranking of casualties among young participants in traffic according to the public risk scope is determined through setting of public risk ranks and classes (Table 2). First, we determined the lowest, and the highest value and scope of the risk and later on we defined the risk classes in-between those two values.

Ordinal No	Level of risk	Public risk			
traffic safety)	(description)	class (interval)	rang (color)		
1	low risk	up to 5,0			
2	low-medium risk	[5,0 – 10,0)			
3	medium risk	[10,0 - 15,0)			
4	high-medium risk	[15,0 - 20,0)			
5	5 high risk				

Table 2. Public risk ranks and classes for threats to young people

Based on the ranking of casualties among young people in traffic that has been carried out in such a way, we can identify and single out the municipalities with the highest public risk, namely the municipalities where undertaking of measures aimed at reduction of traffic threats to young participants in traffic is urgently needed.

#### 3.4. Public risk of casualties among young participants in traffic in the territory of Serbia

According to the above-mentioned criterion, the highest risk of deaths among young people (those aged from 15 to 19) in traffic is present in the territory of municipality of Backi Petrovac and it makes 57.9 of the killed young people per 100,000 young people. A very high risk of deaths among young people is also present in 23 municipalities in Serbia, such as the municipality of Malo Crnice (50.6), Ivanjica (43.1), Prijepolje (42.3), Cajetina (41.9), and Knjazevac (41.4) etc. The municipalities with a very low risk include the municipality of Cacak (4.9), Stara Pazova (4.1), Leskovac (3.9), Novi Sad (2.0), Kragujevac (1.6) etc.

When it comes to threats of casualties among young people aged from 20 to 24 the situation is somewhat different. If we compare Figure 1 with Figure 2 we can see that the number of municipalities with a very high risk of deaths among young people aged from 20 to 24 is much larger (50) than in the age group from 15 to 19 (23). Namely, the highest public risk of deaths has been identified in the territory of municipality of Cajetina – it makes even 114.5. The public risk of deaths is also very high in the territories of municipalities of Velika Plana (83.2), Kanjiza (78.9), Zabalj (63.2), Sremski Karlovci (62.9), Backi Petrovac (61.5) etc. In the territories of those municipalities, the number of casualties among young people per 100,000 of young participants in traffic is far higher than in the territories of other municipalities in the Republic of Serbia.

The graph presentation of distribution of public risk of deaths (Figure 1 and Figure 2) shows the best the threat ratio among young people aged from 15 to 19 and young people aged from 20 to 24. Such presentation also simplifies spotting of municipalities that should be the first to become the "subject" of measures of reduction of threats to young people in traffic.





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#### 4. FINAL CONSIDERATIONS WITH GENERAL PROPOSAL OF MEASURES

In the period from 2002 to 2006, 87.986 of persons were casualties in traffic accidents on the roads in Serbia and 22.185 of them belong to the age group from 15 to 24.

An emphasised number of casualties among young people is not the problem in Serbia alone but in many developed countries of the world as well so that this phenomenon has to be analysed as the problem, which has to be treated as a high priority one within public reactions of the society on the whole. Due to that, the attention has to be paid to special measures that can contribute to reduction of the number of traffic accidents with young participating young drivers.

Local government is always playing a significant role in traffic safety and its responsibilities cover a wide spectrum of social services, from technical to health care and social services. In order to develop an efficient traffic safety programme it is necessary to prepare and conduct a comprehensive analysis of traffic safety, which should be updated periodically (per time intervals during the year, per year etc.).

Some of the measures that should be implemented aiming at improving traffic safety among young people in traffic include:

- Young people are capable of clear spotting, understanding, evaluating, and reacting fast and their memory is sharp and vivid. Therefore, the most efficient measure within social reaction towards the young people is timely and quality preparation for traffic in order to take the advantage and channel properly the advantage that young people posses.
- The introduction of graded driving licence upon legal maturity young people are liable to obtained riving licence for all categories of vehicles, except for buses and trolleybuses. As it has been noted that the system of preparation for traffic does not produce "safe" drivers, it is necessary to prescribed issuing of temporary driving licences with the validity period of two years fro the beginners, which will not allow them to carry out more complex driving tasks.
- The establishment of the Traffic Safety Agency within the Government, which will have the authority and responsibility for decision making, control over resources and coordinate the work of all Government sectors dealing with traffic safety (health care, transport, education and police).
- Preparation of the national traffic safety strategy and action plan traffic safety strategy should take into account the needs of all the participants in traffic, in particular of vulnerable categories and it should be linked with strategies in other sectors. Practically speaking, each municipality in Serbia should pass its own traffic safety strategy in accordance with characteristics obtained through the analysis because its efficiency during implementation may be threatened if it is not the result of concrete analysis.
- **4** To promote educational campaigns designated to young people in traffic.
- **4** To improve and maintain the database on accidents and casualties.
- To carry out and stimulate researches, monitor and implement practices from successful countries.

Such an approach in consideration and further resolving of problems in traffic safety promotes the implementation of further researches in the field of traffic safety at a microlevel, which represents the additional quality in further work related to enhancement of its protection mechanism.

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# DETERMINING THE FLOW OF GOODS WITH THE GOAL OF INCREASE OF EFFECTIVENESS IN CARGO TRANSPORTATION IN THE RIVER-SEA DIRECTION

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#### **Abstract:**

Important place in the process of increase of effectiveness in cargo transportation by waterways are reserved for direct river-sea transports. This refers to transports between places on inland waterways and sea ports. This is the reason why, in order to improve this means of transport, it is necessary to determine technical and economic factors, which determine suitability of this means of transport. Determining the flow of goods is one of the most important factors.

Serbia is a country with very favourable transport-geographical position considering that the shortest road and rail corridors between countries of Western and Central Europe and Southern Europe and Middle and Far East go through its territory. International waterway Danube flows 558 km through Serbia, connecting the North Sea and the Black Sea through canal Danube-Main. Due to this well-located transport-geographical position international freight transport on pan-European corridors VII and X has been constantly increasing.

The goal of this paper is to determine the total flow of goods for Serbia, as precisely as possible. From this information potential flow of goods on river Danube - sea direction can be set aside.

Key words:

Flow of goods, river ports, sea ports, river-sea vessel.

# **1. INTRODUCTION**

The goal of this research is to display data on transport of goods on our inland waterways. This research provides the data on economic, technical and geographical characteristics of transport and traffic of goods. Additionally, the following indicators are also obtainable: types and carrying capacities of vessels, vessel flags, places of loading and unloading of goods, countries of loading and unloading of goods, types of transport and amounts of transported goods. Moreover, this research offers the data on domestic and international goods flows by ports of loading, unloading, as well as data on vessel flags.

The data from this are used for presenting overall volume and structure of goods traffic on inland waterways, as well as for comparing the goods traffic on inland waterways with the traffic done by other modes of transport. Statistic of inland waterways transport enabled comparison with corresponding statistics of other Danube countries, received from the Danube Commission, with headquarters in Budapest.

The data collected through this research are also used for calculating global statistical indicators, such as physical volume index of transport services. The obtained results are sent to international organizations dealing with transport, such as The Danube Commission, UN ECE-inland transport committee, Organization for Economic Cooperation and Development (DUNCOM, UN ECE-IT and OECD), etc.

# 2. TOTAL INTERNATIONAL FREIGHT TRANSPORT

Total international freight traffic in the period 1996-2006, annually increased by 10.8% on average. Export of goods realized by all transport modes, grew with the average rate of 10.9%, import with the rate of 6.7%, and in this period the highest increase rate of 12.8% was noted in



transit. Considerably higher growth rate were noted in the period 2001-2006, in comparison with the period 1996-2000. It is understandable taking into account that in 1999 Serbia was being destructed by NATO aviation. As a consequence, rail and inland waterway networks were particularly damaged. In the period 2000-2006 total international freight traffic increased at the annual rate of 20.3%. Export of goods grew at the rate of 15.9%, import at the rate 13.6% and transit at the rate of 34.4%. Although transit of goods performed by all modes of transport showed extremely dynamic growth rates in this period, it was noticed that the highest growth rate, with the reconstruction of our waterways, was recorded in inland waterways transit of goods.

In 2006, majority of total goods conveyed by all modes of international transport were transported by road freight vehicles, around 42.9%, 21.8% were transported by inland waterways, and 23.0% by rail transport and 12.3% is the share of oil and gas transported by pipelines. Looking back to 1996, it can be noticed that the largest amount of goods was carried by inland waterway transport (49.2%), followed by road transport (28.5%). In the same year the share of rail transport in total international freight transport was 14.1% and 8.2% was the share of pipeline transport.

#### 2.1. Export of goods by modes of transport

Total export of goods realized by all modes of transport in the period 1996-2006 grew at the average annual rate of 10.9%. The highest growth rate in this period was registered in rail transport (15.4%); a little bit slower increase was noted in road transport (12.8%) and the slowest raise of 3.6% was in inland waterways transport. Significantly slower growth rate of 3.8% in export was noted in the period 1996-2000, in contrast to the period after 2000, when the export increase rate was 22.9%.

Comparing different modes of transport, it is apparent that from 2000 to 2006, the fastest export increase was in rail transport, as it increased almost four times during this period, road transport increased about 2.5 times and inland waterways transport more than 2 times. Share of road and rail transport in total export increased during the period 1996-2006, unlike inland waterway transport whose share dropped from 35% to 17.9% in 2006.

Export of goods to European countries in 2006, compared to 1996, a year before the NATO aviation aggression, was over three times higher. Transport by rail was almost four times higher, transport by road three times and inland waterways transport over two times higher.

Compared to 2000, total export of goods to European countries, done by all odes of transport, was almost three times higher, where a fast growth over five times was noted in rail freight transport.

Total export of goods to the EU countries in the period 1996-2006 increased by 3.8 times, but with different progress rates in various modes of transport. Thus the rail freight transport in the observed period was almost 14 times higher, road transport 3.8 times higher and inland waterway transport by 22.3% higher.

Total export to EU member states in 2006, compared to 2000 was over 3.7 times higher, where the fastest rise of over 11 times was recorded in rail transport. In the same period export of goods to EU member states by road increased 2.6 times and export by inland waterway transport 2.5 times.

Total export of agricultural product realized by all modes of transport in 2006 was 1782 thousand tons, whereof cereals made over 68%. Export by road made more then half of total amount of exported food products, export by inland waterways almost two fifths, while the rest was exported by rail. Export of metal products was 1463 thousand tons, of which the largest share of 657 thousand tons comprised plates, wires and other construction materials for railway tracks. Over two fifths of the products from this group were transported by rail.

The export of machinery, transport equipment, manufactured goods and miscellaneous articles was 1379 thousand tons, where four fifths of the goods were transported by road. The export of crude and manufactured minerals and building materials was 895 thousand tons and majority of it, almost two fifths was transported by inland waterways.

#### 2.2. Import of goods by modes of transport

Total import of goods realized by all modes of transport in the period 1996-2006 noted a slight slower rate in comparison to export growth rate. In the referent period, average growth rate of import was 6.7% while the highest increase rate of 13.7% was noted in pipeline transport. Road transport recorded annual growth rate of 7.0% and rail transport of 5.9%. Compared to other transport modes, the lowest growth rate of only 1.5% was noted in inland waterway transport.

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In the period 2000-2006, overall import of goods was 2.1 times greater. The fastest growth rate of almost eight times was recorded in pipeline transport, mainly because of the reuse of oil pipelines from Omisalj (Croatia) to our refineries in Novi Sad and Pancevo. In the same period, rail transport increased by more than two times, road transport by 67.6% and the lowest increase of 30.4% was noticed in inland waterway transport.

Total import of goods from European countries in the period 1996-2006 increased almost two times with equal growth rates in all modes of transport. Therefore, rail transport to European countries in the observed period was two times greater, inland waterway transport more than two times and road transport almost two times.

In the same period import of goods from the EU member states increased three times and transport of goods by road increased over three times. Import of goods from the EU by inland waterways was the only mode of transport with negative trend, meaning that it decreased two times. In 2000, 79.6% of total goods from the EU countries were imported by road transport and the rest by rail and inland waterway transport. Six years later, in the trade with the EU, road transport was still a dominant mode of transport, as almost three fifths of total goods, for our economy needs, were transported by road. A third of the goods were transported by rail, only 4.8% by inland waterways and 3% by pipelines (natural gas from Hungary).

Almost two fifths of the total import of 15723 thousand tons referred to crude oil and its products. Import of crude oil was 2222 thousand tons; import of gas was 3333 thousand tons, while amount of imported refined oil products was 420 thousand tons. The largest amount of this type of goods was imported by pipeline transport (over four fifths), followed by rail and inland waterway transport. Import of ores and metal waste was 1929 thousand tons and import of solid mineral fuels was 1594 thousand tons.

The largest amount of imported ores and metal waste was carried by inland waterways, 88,5% and share of this mode in solid mineral fuels import was considerably small, taking into account the composition of goods (a fourth of total import was transported by inland waterways). This group of goods was mostly conveyed by rail, over three fifths of the total quantity. Imported metal products were mostly carried by road, 45.1% and by inland waterway transport 19.7%. Referring to the import of machinery, transport equipment, manufactured goods and miscellaneous articles, 40.8% of total goods were transported by road and a third by rail transport.

# 2.3. Transit of goods by modes of transport

Total transit of goods over the territory of Serbia, related to all transport modes, increased by 3.5 times in the period 1996-2000. The fastest increase was recorded in goods transported by road vehicles, while slowest increase was noted in inland waterway transport, i.e. transport on the Danube.

Out of 17555 thousand tons carried in transit by rail, road and inland waterway transport in 2006, 4037 thousand tons were transferred from and to Turkey via our transportation network, out of which 75% was transported by road vehicles. In goods transit to and from Bulgaria, 3876 thousand tons were carried, out of which 57.8% by road, 32.0% by rail and 10.2% by inland waterways. In goods transit to and from Greece, over Serbian transportation network, 2137 thousand tones were transported, whereof 46.1% by road and 53.9% by rail. Total transit between Germany and Serbia was 3324 thousand tons of goods and between Serbia and Romania 2974 thousand tons.

# 3. INLAND WATERWAYS TRANSPORT

Besides the Danube, the international rivers Sava and Tisa with their tributaries and navigable canals provide 1360 km of navigable waterways for the ships with carrying capacity of up to 400 tons. The majority of ports in Serbian part of the Danube, after the construction of the big dam have been equipped to provide docking for smaller river-sea boats. This significant improvement in navigation enables direct transport between Serbian ports on the Danube and the sea ports on the Black and Mediterranean Seas, without reloading in ports situated in the delta of the Danube.

After years of stagnation due to the destruction of the bridges on Sava and the Danube (1999), building of new and reconstruction of old bridges, as well as after clearing of waterways, regular navigation through Serbian part of the waterways to the Black Sea was enabled. Building of the waterway Danube-Main-Rhine facilitated successful connection of river ports on the Danube with the ports in The Rhine river basin and the Northern Sea ports. Building of the



navigable canal Cherna Voda-Constanta shortened the waterway to the Black Sea for over 200 km. Total international goods transport by inland waterways in 2006, compared to 1996 increased by 11.7%, with slightly more dynamic increase of export (43.2%) and import (16.8%). Nevertheless, in the period 2000-2006, after clearing the waterway network, total international inland waterways transport increased by more then 3.5 time, where extreme rise of more then 16 times was noted in transit transport of goods.

#### 3.1. Export of goods by inland waterways

Somewhat more then fifth of the total amount of goods exported by inland waterways in 2006 was carried to the EU member countries. 15.8% of the total export to the EU was carried to Germany on waterway Danube-Maine-Rhine. Three fifths of the total goods in export were exported to the river-sea ports on the Black Sea, out of which, more then a half was transported through reloading into sea boats, to the countries of the Black Sea region. By reloading to sea boats, majority of goods were exported to Italy, Spain and non-European countries.

Less then one fourth of the total 1472 thousand tons was transported by Serbian boats. The largest amount of the exported goods was carried by Ukrainian and Romanian boats.

#### **3.2. Import of goods by inland waterways**

Only 18.4% out of the total of 3406 thousand tons imported to Serbian ports were carried by Serbian boats. Not even a single ton was carried by Serbian boats in external trade with Austria and Slovakia. It is interesting that vessels of all other countries of the Danube region except Serbia were included in goods import trade with Austria. Only 157 thousand tons of goods were imported from the EU countries. The largest quantities of goods were imported from the river-sea ports in the lower basin of the Danube. Hence, 1693 thousand tons were imported from Romania and 1516 thousand tons from Ukraine. However, only 282 thousand tons of goods imported from Romania were of Romanian origin.

Referring to 2006 export, agricultural products presented the major part amounting to 51.2% of the total export. Cereals had the largest share in export form this group, 98.1%. Export of crude and processed minerals was 330 thousand tons, whereof cement and lime made 16.3%. In the same year, 248 thousand tons of metal products were exported. Almost half of it referred to steel plates.

During 2006, over 500.0% of the imported goods related to ores and mineral waste, whereof 94.8% was iron ore. 409 thousand tons of solid fuels were imported, 376 thousand tons of metal products and 362 thousand tons of fertilizers.

#### 3.3. Transit of goods by inland waterways

In 2006, 4146 thousand tons were carried in transit over the Danube. The largest amount of goods was loaded in Ukraine, 40.0%, then in Romania, 12.4% and in Bulgaria 7.8%. 10.8% of the goods in transit were loaded in the countries outside the Danube river region, carried over Serbian waterways for unloading to the countries of the Black Sea region.

In the same year, the largest quantity of goods carried by the Danube in transit through territory of Serbia was unloaded in the EU countries, about 63.8%. 65.5% of the total goods unloaded in the EU were unloaded in Austria and about 25.3% in Germany.

The largest volume of goods flow in transit was between Ukraine and Austria, 27.9% of total transit. Also significant goods flow in total goods transit by inland waterways of the Republic of Serbia were done between Ukraine and Croatia, as well as between Romania and Austria, with shares of 13.4% and 12.3% respectively.

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# VACUUM IMPREGNATION PRETREATMENT OF FRESH CUT VEGETABLE

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#### ABSTRACT

Vegetal products are generally characterized through a high level of sensitivity due to environmental factors and to the operations they are submitted to during their preparation. This leads to meaningful changes regarding vegetal products nutritional and sensorial characteristics. The prevention of such drawbacks can be made by introducing active compounds in their structure in order to protect them from unwanted alterations. The introduction of compounds can be achieved through classical infusion, through the immersion of the products in hypertonic solutions of the respective compound, or through a new technology, vacuum impregnation. In this paper, we present the data obtained during the experiments regarding impregnation whit some nutraceutical under a 500 mbarr vacuum of some vegetables, evaluated through physical and chemical proprieties.

# **1. INTRODUCTION**

The increasing interest of people for the consumption of foods that have a beneficial effect on health has oriented both the research and the production in food industry towards the goal of obtaining such products<sup>1</sup>. Due to this fact, one of the main directions in the alimentary industry is focused upon the preservation of the existing natural compounds either through the minimum processing of the raw materials or through the strengthening of the foods with multiple physiologic active compounds such as prebiotics, probiotics, vitamins, fiber, mineral salts etc<sup>2</sup>.

Another possibility to introduce the compounds in the structure of vegetable products, especially in the internal structure of fruit and vegetables, consists in the usage of a new technology, vacuum impregnation.

Vacuum impregnation consists in the immersion of vegetable products, characterized through high porosity (apple, quince, strawberries, apricots, peaches, peppers, mushrooms, etc), in solutions which contain dissolved substances meant to impregnate the product, followed by their storage in a place under a certain void pressure<sup>3</sup>. This technology can be applied in order to better the texture of the product to reduce its level of oxidation and its exudates at defrosting, to maintain its color, and to strengthen the different vegetable products with all kinds of nutrients: vitamin E<sup>4</sup>, minerals salts like Ca and Zn<sup>5</sup>, probiotics<sup>6</sup>.

The aim of this paper is to use vacuum impregnation in order to introduce ascorbic acid into the structure of apples, so that the products become strengthened with vitamins and follow the vitamin's stability during the storage of apples in terms of refrigeration and defrosting<sup>7</sup>. We also took into account the need to prevent the sliced apples to turn brown during this process, knowing their sensitivity towards oxidative factors on the one hand and the antioxidant properties of ascorbic acid<sup>8</sup> on the other hand.

# 2. THE STUDY Materials and methods

Golden Delicious apple were purchased from a local store.



The following instrumentation has been used: installation for impregnation under void which consists in a RL-2 void pump and a vacuum-meter - manufactured by REFCO Manufacturing Ltd. from Switzerland- linked to a void exicator.

For impregnation we used a 0.5 per cent ascorbic acid (Fluka CH 9470 Buchs) solution.

The dosage of vitamin C was realized by iodomethric method<sup>9</sup>, using solutions of potassium iodide 1 per cent and potassium iodate n/1000.

#### Experimental

The healthiest products have been chosen for the experiments, they were washed, their seeds and the seed home were removed with an stainless tubular knife and afterwards they were pealed off and cut in round shapes with the help of an stainless knife. The round circles had between 7 and 10 mm and a mass between 11 and 13.5 g. The samples were immersed in a solution in order to avoid their contact with the the air, apples sensitivity towards oxidation being a well known feature.

For impregnation we used a 0.5 per cent ascorbic acid solution.

For impregnation at atmospheric pressure, the apple slices were immersed within the solution. When the time expired, the apples have been removed from the ascorbic acid solution, they were put on a filter paper in order to obviate excessive water. One of the samples was used in order to dosage the vitamin C, while three other samples have been placed in glass containers and stored in the absence of light under refrigeration at 4 oC. Vitamin C has been dosed after three, six and nine days.

Two samples were kept under refrigeration at -180C. In this case, the dosage of vitamin C was done after 9 and 14 days.

For vacuum impregnation, the apple slices were immersed in the solution, introduced in the void exicator and maintained at a 500 mbarr vacuum pressure for 10 minutes. When the time expired, the apples have been removed from the solution; they were put on a filter paper in order to obviate excessive water. We calculated the quantity of impregnated solution and expressed it in percentage. A sample was used immediately for determination of vitamin C and three samples were placed in glass containers and stored in the absence of light under refrigeration at 4 oC. Vitamin C was dosed after three, six and nine days.

Two samples were stored in a freezer at -18°C. In this case, the dosage of vitamin C was done after 9, and 14 days. The dosage of vitamin C was done using an iodomethric method. The method was chosen because it is simple and quick, it can be used for uncolored products, if we want to do some tests in order to obtain comparative results for products of the same species. The method is based on ascorbic acid oxidation with iodine produced through a reaction between potassium iodide and potassium iodate in an acid environment.

From an average sample made of examined material 10-20g is taken. The weighing are done using a analytical balance. The weighted material is grinded in a mortar with a bit of hydrochloric acid 2 per cent and 5 d of quartz sand, until a homogeneous paste is obtained. 40-50 ml dilution of hydrochloric acid 2 per cent is added and after a short mixing it is left to settle aut for e few minutes, then is filtered in a measuring bottle of 100 cm<sup>3</sup>. The material remained in the mortar is washed 3-4 times with hydrochloric acid 2 per cent levigating and filtering the dilution and washing the measuring bottle. Thenceforth it is brought to the sign with hydrochloric acid 2 per cent and strongky stirred.

In an Erlenmayer of 100  $\text{cm}^{3}$ , 10  $\text{cm}^{3}$  of the obtained extract is instilled, 30  $\text{cm}^{3}$  of distilled water, 5  $\text{cm}^{3}$  of potassium iodide 1 per cent and 5  $\text{cm}^{3}$  of starch glue 0,2 per cent as an indicator are added. It is titrated using potassium iodate n/1000 up to dark blue persistent 30 seconds.

The calculation results: VitaminaC =  $\frac{V \times V_1 \times 0.088}{G \times V_2} \times 100$ 

where:

- V potassium iodate volume n/1000 for titrating [cm<sup>3</sup>];
- $V_1$  extract volume [cm<sup>3</sup>];
- $V_2$  semples volume [cm<sup>3</sup>];
- G Weight of the analyzed sample [g]; Each measurement was taken in duplicate.



# 3. ANALISES, DISCUSION, APROACHES, INTERPRETATIONS

The results which were obtained after the dosage of ascorbic acid for the analyzed samples are listed in Table 1 and Table 2.

Table1. The content of vitamin C in the apples impregnated with a solution of ascorbic acid 0.5 per cent at atmospheric pressure and under vacuum after the preservation under refrigeration.

Nr.	Sample	Vitamin C content [mg/100g product]					
crt.	Sample	To	$T_1$	$T_2$	T <sub>3</sub>		
1.	Control	6,47	3,92	-	-		
2.	Sample impregnated at atmospheric pressure and refrigeration	36,03	12,09	8,55	5,92		
3.	Sample impregnated under vacuum and refrigeration	81,46	73,05	62,41	37,26		

 $T_0$  = immediately after impregnation,  $T_1$  = 3 days,  $T_2$ = 6 days =,  $T_3$  = 9 days

Table 2 The content of vitamin C in the apples impregnated with a solution of ascorbic acid 0.5% at atmospheric pressure and under vacuum after the preservation under freezing.

Nr.	Samplo	Vitamin C content [mg/100g product]				
crt.	Sample	To	$T_4$	$T_5$		
1.	Sample impregnated at atmospheric pressure and freezing	37,29	31,42	30,45		
2.	Sample impregnated under vacuum and freezing	79,84	72,96	72,47		

 $T_0$  = immediately after impregnation,  $T_4$  = 9 days,  $T_5$  = 14 days

This study shows that by the vacuum impregnation of apples, Figure 1 (in certain work conditions) the content of ascorbic acid can be increased by 55% compared to the atmospheric pressure impregnation.

A reduction of ascorbic acid degradation has also been observed regarding the samples which had been impregnated under vacuum, compared to samples impregnated at atmospheric pressure, in the cases of preservation under refrigeration as well as the preservation in freezing conditions. Thus:

- after 3 days the sample impregnated under vacuum reduced its content of vitamin C by only 10.32% while the sample impregnated at atmospheric pressure reduced its Vitamin C content with 33.5%;
- 4 after 6 days the sample impregnated under vacuum reduced its content of vitamin C by only 23.38% while the sample impregnated at atmospheric pressure reduced its Vitamin C content with 76.27%;
- 4 after 9 days the sample impregnated under vacuum reduced its content of vitamin C by 54.26% while the sample impregnated at atmospheric pressure reduced its Vitamin C content with 83.56%;



Fig.1 Vitamin C content in fresh cut apples after refrigeration



The growth of ascorbic acid content and its higher stability can be explained by the fact that under vacuum impregnation the ascorbic acid penetrates into the plant tissue replacing the air (oxygen) from the apples porous structure.



By keeping products in frozen state, as was expected, the stability of vitamin C is higher (Figure2) than by preserving the products refrigerated. Nevertheless in this case the vacuum impregnation content of vitamin C was reduced by only 8.61% after 9 days and 9.22 after 14 days, in comparison to impregnation at atmospheric pressure where the reduction was of 15.7% after 9 days, respectively with 18.34 after 14 days.

## 4. CONCLUSIONS

Vacuum impregnation allows the ascorbic acid to incorporate itself in the structure of the apples in a much higher quantity than under atmospheric pressure. At the same time, vitamin C, impregnated under vacuum, has a greater stability in time due to the absence of oxygen.

Impregnation under vacuum thus presents a great potential of strengthening porous plants with other nutrients intended to improve their nutritional characteristics and also with compounds that can have a positive effect upon their physical or sensorial characteristics.

The sensorial evaluation of products impregnated under vacuum is particularly important in order to observe their degree of acceptance by consumers, task with which we shall continue these studies.

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# ENVIRONMENT ECOLOGICAL PROCESS IN HUNEDOARA AREA THROUGH REINSERTION IN ECONOMIC CIRCUIT OF SCRAP AND PULVEROUS WASTE

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#### **ABSTRACT:**

The Hunedoara area, from industrialization viewpoint is placed before 1989 on 3 places after Bucuresti and Brasov. Representative was the iron and steel, energetic and mining industries. Through specific technological process, besides the main products have output a series of residues, that in 95% from cases were deposited on dumps and ponds.

In paper is presented a synthesis of results obtained of authors regarding to reinsertion in the economic circuit of scrap and pulverous waste existing in Hunedoara area.

Through these capitalization of wastes in the iron and steel industry I done substantial economies in cost-price of final product, on aside, and but the other side are in progress an ecological process of environment Hunedoara area through give back of occupied surfaces with these waste to the natural frame.

## **KEY WORDS:**

waste, recycling, siderurgy, pollution, industry

# **1. INTRODUCTION**

A long and hard process of industrial restructuring for Romania began in 1990, which influenced directly the quantity of industrial wastes produced in the country, their content and their possibilities of recycling. In Romania and in the other former socialist countries the inefficient management and the operation of the productive assets under the pressure of some unachievable objectives led to the interrupted functioning of the production and to the inadequate management of resources, contributing to excessive pollution levels and generating a huge volume of industrial wastes.

The sustained development of the heavy industry combined with the intensely subsidized energy and the unjustified low prices of the raw materials led to a very low efficiency of the energy use, the extensive use of the natural resources and the production of some great waste quantities. In the region where we propose the recycling of the small and pulverous wastes there are found great quantities of such wastes proceeded from the steel, energetic and mining industries.

Among the industrial branches some are responsible for producing most of the wastes: coal and ore extraction and preparation, producing the energy, the metallurgy, the chemistry, etc. For the industrial products whose fabrication implies generating of great quantities of wastes, such as: coking coal, crude iron and crude steel, the physical production had a general decreasing tendency. At these products, a tendency of production stabilization at levels of about 30% of those recorded in 1989 is found [1].

From a theoretic point of view, the industrial waste volume produced depends directly of the physical production volume (less of its value). The industrial waste quantities that are reported in various publications and studies are not correlated very well with the physic volume of the industrial production in Romania (there is not respected the discipline in financial administration and technology).



In Romania, like in other countries, the waste impact upon the environment has increased alarmingly in the latest years, their uncorresponding administration generating the contamination of the soil and of the ground water and also emissions of methane, Carbon dioxide and noxious gases, having direct effects upon the population health. The storage spaces have arrived to saturation and finding other mew ones has become a major problem (in the context of privatization).

For Romania the waste recycling represents a priority of the strategy of lasting development from the following reasons:

- the natural resources at some categories of raw materials are poor and insufficient, the industrial processing of the poor resources is made in non-competitive conditions or at the limit of competitiveness, the import of complementary raw materials can be carried out only within the limit allowed by the current account balance;
- complementing the resources by recycling the wastes can be achieved with lower costs, as a result of the significant economy of specific consumptions of energy, water, other materials, labor and of the important reduction of pollution and mining wastes in comparison with the useful substance extraction from the ores.

In the countries having a developed steel industry, the ferrous pulverous wastes are practically used in a ratio of over 90% by their reintroduction in the steel industry circuit. From the study of the specialty literature it results that for their practical application several technologies are practiced, namely: practical application by sintering, practical application by pelletizing, practical application by briquetting, practical application by reduction without any initial processing, practical application by the CARBOFER method.

## 2. THE STUDY

The paper presents CARBOFER obtain in the shape of micropellets, the recipes suggested for experimentations in laboratory phase following the obtained of a recyclable product, usable as well as a slag foaming agent in the process of steel made in electric furnace as well as with component in agglomeration.

The recipes for the micropellets production were thus established that the obtained micropellets to can be used-up one in two processes previously mention; therefore there must have the following characteristics:

- the recipes components granulation (for laboratory phase experimentations) must to correspond for pelletizing process (respectively granulometric structure of the palletizing charge [2,3]);
- the Fe<sub>total</sub> contained must be is in the existing limits of in the used-up ores to agglomeration;
- the Carbon contained must to assure necessary of reducer element in case of using this product as slag foaming agent, and in case of using this product in agglomeration process of, must to fractionally replace an amount of coke from charge;
- contained of CaO must to assure, beside bentonite, the cementing material in order to obtaining adequate micropellets (incompressible) from behavior viewpoints to handle, transport and in the technological process.

The CARBOFER chemical composition (in micropellets shape) it's presented in table 1. Table 1. CARBOFER (micropellets form) chemical composition

Pagipo					Recipe	compone	nts, [%]				
no.	$SiO_2$	FeO	Fe <sub>2</sub> O <sub>3</sub>	$P_2O_5$	S	С	$Al_2O_3$	CaO	MgO	MnO	Other oxides
R1	6,74	3,97	38,32	0,10	0,44	13,94	3,53	20,98	1,14	1,37	9,47
R2	7,45	3,97	38,34	0,10	0,44	14,92	3,65	19,10	1,13	1,36	9,53
R3	9,01	3,83	32,68	0,09	0,47	19,19	4,06	18,38	1,19	1,16	9,93
R4	8,45	4,11	34,94	0,10	0,49	17,59	4,06	17,54	1,20	1,19	10,34
R5	8,15	4,11	40,10	0,10	0,44	14,92	3,76	16,25	1,11	1,37	9,68
R6	8,37	4,19	36,38	0,10	0,48	18,39	3,98	15,53	1,15	1,19	10,24
R7	7,80	4,34	34,19	0,09	0,50	21,69	4,00	14,68	1,16	1,04	10,51
R8	7,89	4,28	33,60	0,09	0,51	22,84	4,08	13,81	1,17	1,07	10,66
R9	8,03	4,41	33,25	0,09	0,53	21,24	4,21	14,93	1,22	1,04	11,04
R10	8,03	4,59	36,79	0,09	0,53	20,26	4,20	12,05	1,19	1,14	11,14

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After micropelletizing process, for each charge was determinates the following characteristics:

- the micropellets bulk weight, wet and dried state [kg/dm<sup>3</sup>];
- the micropellets humidity, [%];
- **the micropellets, raw state distribution on granulometric classes.** 
  - The results are presented in table 2.

								Granulometric classes, [mm]							
Recipe no.	Reci	pe comj	ponents	,[%]	Humi- dity, [%]	Iumi- dity, [kg/dm <sup>3</sup> ] [%]		>5 + 5÷3	>5	5÷3	3÷2	2÷1	<1	3÷1	3÷1 + <1
	Fe	CaO	C	$Al_2O_3$		wed	dried		(	Franul	ometri	c analy	sis, [%	]	
1	29,91	20,98	13,94	3,53	3,96	1,26	1,21	73	27	46	15,5	11	0,5	26,5	27
2	29,93	19,1	14,92	3,65	4,96	1,21	1,15	61	9,5	51,5	22,1	15,2	1,7	37,3	39
3	25,86	18,38	19,19	4,06	2,44	1,23	1,2	15	6,5	8,5	10,5	73,5	1	84	85
4	27,66	17,54	17,59	4,06	4,9	1,02	0,97	17	5	12	18	63,5	1,5	81,5	83
5	31,27	16,25	14,92	3,76	3,94	1,27	1,22	38	6	32	18,5	30,5	13	49	62
6	28,73	15,53	18,39	3,98	3,67	1,09	1,05	20,5	2	18,5	39	38	2,5	77	79,5
7	27,73	14,68	21,69	4,00	3,45	1,16	1,12	76,5	63,5	13	9,5	12	2	21,5	23,5
8	26,85	13,81	22,84	4,08	4,39	1,14	1,09	11,5	1,5	10	22,5	62,5	3,5	85	88,5
9	26,71	14,93	21,24	4,21	4,84	1,24	1,18	49,5	21,5	28	22,5	17,5	10,5	40	50,5
10	29,32	12,05	20,26	4,2	2,86	1,07	1,02	8,5	1	7,5	22	41	28,5	63	91,5

# Table 2. The main characteristics of micropellets

# 3. ANALISES, DISCUTIONS, APPROACHES, INTERPRETATIONS

In figure 1 its presented appearances from palletizing process (with a laboratory dish pelletizing installation) and the obtained micropellets, base on micropellets CARBOFER technological flux.



Figure 1. Aspects from CARBOFER technological process

From viewpoint of the three main components: Fe, C, Ca, we have determinate that is covered the whole variation interspaces (area), what demonstrates the method flexibility, through the possibility of choose which recipes can contain one or many pulverous residues, dependency of the enforced chemical composition for recycling the obtained products (steelwork or agglomeration process), as the amount of residues generate in currently way on a certain distance, as well as depending on the amount of pulverous residues (inclusively small once) stored in ponds (placed around of the unit which generates the pulverous residues).

## 4. CONCLUSIONS

From the results analysis, we considered as the optimum recipes, from viewpoint of granulometric composition (that must to satisfy the condition of uniformity and prevalent in



1-3mm limits - granulation recommended as much in the steelwork process as slag foaming agent as well in agglomeration process), the recipes no. R3, R4, R6, R8.

Analyzing the results obtaining in the wake of our experimentations, is recommended the CARBOFER utilization as slag foaming agent and used at the electric furnaces, no influencing the steel and slag chemical composition.

Also, by utilizing CARBOFER, we obtained economic and ecological effects, through the rendition busy surfaces with these residues to the natural frame.

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# POSIBILITY TO RECYCLING OF DEFERRIZED STEELSHOP SLAGS IN AGRICULTURE

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#### **ABSTRACT:**

The use in agriculture of the deferrized slag allows the development of some existing methods regarding the influence of the slag addition in the soil upon the plant growing and development. The proposed technology does not generate other pollution sources and it is efficient from the economic point of view, it can be implemented in practice either by the producers of such wastes or by other firms using deferrized slag. The use in other sectors of the steel shop slag leads to release the surfaces occupied by these wastes and to render them to the respective natural landscape, there takes place a reduction of the pollution degree in the regions having steel industry.

#### **KEY WORDS:**

slag, recycling, agriculture, pollution, industry

### **1. INTRODUCTION**

The siderurgic industry produces a series of specific wastes (slags, iron scales, dust and furnace slime, electro filter dust from steel plants, et.) which are recovered in a very reduced proportion, the remainder being deposited in dumps and clarifying) settling ponds. Considering the iron contents and the fact that without recovery, they are a source of pollution for the environment (water, air, soil), there is a need to find solutions to process them, in order to be brought to a favorable state for use as raw or auxiliary material in the metallurgical field or in other sectors of economy. The most adequate solution adopted for ferrous waste extraction from slags is the electromagnetic ore, after a proper sequence of crushing and sorting of the slag. At the present moment, these slags are successfully used in siderurgy, agriculture and constructions.

Processing steel plant slags is beneficial for environment protection, community and agricultural welfare as well as from the technical point of view: metallurgical slags are nontoxic materials, with physical and chemical properties that are similar to rocks, so they represent a viable alternative, sometimes preferable to the natural variants for usage in constructions.

The activity of metallurgical slag processing meets the requirements of environment protection and the European Directives related to environment protection, stipulated in Law 73/2000, republished with the further alterations and completions. From this point of view, metallurgical slag processing aims, directly and indirectly, at two targets included in the community acquis: the control and reduction of soil pollution by using clean technologies involving the turning of metallurgical slag wastes into recycled materials to be used in several domains: road and railway construction, hydro-technical and civil constructions, in the cement, glass and refractory materials industry, as well as in agriculture (improving soil acidity and re-mineralizing it).

According to the available data related to the slag dump at Buituri, the first deposits were made in year 1967 the in the area known as "the old slag dump", and reached an average elevation of 255 m (fig.1). The latest information shows that, at this moment, the maximum dumping elevation at the slag dump in Buituri (fig.2), in on average 340 m, and its area of about 80 ha, which sums up to about 100 million ton of slag deposited next to the old dump. The chemical composition of steel plant slag from Buituri is presented in fig.3.





Fig.1. The old slag dump

Fig.2. The slag dump in Buituri

chemical composition, %								
SiO2	18.38							
Р	<b>0.56</b>							
s	¥0.2							
MgO	9.2							
CaO	35.5							
AI2O3	6.53							
MnO	6.83							
Femet	6.66							
Fe2O3	5.94							
FeO	11.39							
Fetot	<b>119.3</b>							

Fig.3. Chemical compositions of slag from slag dump Buituri

The experiments, which are to be put into practice, aim a use of de-ferromized slag in the agricultural area. Following the industrially obtained results and the economic calculi, the producer may choose either the proposed technologies to be put into practice or to co-operate and support other metallic waste processors.

# 2. THE STUDY

In order to obtain the slag powder needed in the pilot experiments, the ferrous slag was processed in the laboratory of the Faculty of Engineering of Hunedoara.



Fig.4 The screening installation "Analysette 3" Fritsch, the grain size 25µm-2mm

Laboratory experiments have been carried out in the Laboratory of Ore Preparation, which is endowed with an installation of screening, grinding, and magnetic separation.

The steel plant slag was screened, using the jigger for the grain size of 10-50mm respectively the screening installation shown in fig.4. The steel plant slag was crushed in the Kollergang mill and for the magnetic separation we used the belt-type magnetic separator.

Figure 5 shows the percentage distribution for the types of metallic waste, ferrous, respectively non-ferrous slag, resulted from the processing of the steel plant slag.

 $25\mu$ m-2mm The slag powder obtained by crushing the non-ferrous slag (the grain size fractions 0-0,4 mm) was packed in sacks and shipped to the experimental lots in Commune Peştişul Mic.

As to the quality characteristics of the products we obtained, the chemical structure of the resulting slag powder is given in figure 6.





Fig.5. The percentage distribution for the types of metallic waste, ferrous, respectively non-ferrous slag

In parallel with the slag processing operations. we decided upon two experimental lots (one experimental lot plowing land, respectively one experimental lot – grazing area). Also, depending on the quality of the soil and its destination, we decided upon the surface of the experimental lots, which is given in table 1. The limits of the agro-chemical plots were determined according to the degree of complexity of the relief and the top soil.



Fig. 6 The chemical structure of the slag powder

		Table 1.	
No.	Experimental lot	Area	The surface [m <sup>2</sup> ]
1	Experimental lot – plowing land	Peştişul Mic	400
2	Experimental lot – grazing area	Peştişul Mic	100

The experimental lots have a slightly acid pH reaction. It is required that they should be treated and acidity reduced. In order to do that, calcareous addings are necessary. Taking into consideration the theme of the project, we will use powdered non-ferrous steel plant slag. The dosage of the addition quantities has been calculated by the project research team and the result consisted of three experimental values:  $0.4 \text{kg/m}^2$ ,  $0.5 \text{kg/m}^2$  and  $0.6 \text{kg/m}^2$ . As ammonium nitrate favors the increase of soil acidity, it is recommended that fertilization should be done with chemical fertilizers based on nitro-limestone or with complex ternary ones. As to the content in phosphorus of the experimental lots, the chemical analyses showed that they have an average content. The administration of phosphorus has to be associated with nitrogen and potassium. It is recommended that acid soils be fertilized with phosphorus on an annual base. The content of potassium is in deficit on the surfaces under study, its values being extremely low. According to experts, pastures are great potassium consumers. For maximum efficiency, it is recommended to apply potassium alongside with nitrogen and phosphorous. The lots under analysis have average amounts of humus.

The content of nitrogen, established according to NI (nitrogen index) calculated according to the content of humus and the saturation degree of bases shows average values.

Table 2 shows the experimental recipes (the doses of additive – slag powder) and the doses of chemical fertilizers needed by the experimental lots in order to grant their productive potential. For comparison reasons we also considered a witness lot (with no slag additive).

				Table 2.				
No.	Experimental lot		Slag powe	ler, kg/m²	Chemical fertilizers, kg/ m <sup>2</sup>			
		Recipes	Recipes	Recipes	Recipes	р	K	N
		1	2	3	4	1	К	IN
1	plowing land -A	0	0,4	0,5	0,6	0,0058	0,007	0,0142
2	grazing area - P	0	0,4	0,5	0,6	0,0054	0,008	0,0147

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## 3. ANALISES, DISCUTIONS, APPROACHES, INTERPRETATIONS

## Pilot Researches – plowing land

In order to enable the pilot researches, the experimental lot – a plowing area of  $400m^2$  was divided into four plots: A1-A4 shown in fig.7.

A1	A2	A3	A4
Surface 100m <sup>2</sup>	Surface 100m <sup>2</sup>	Surface 100m <sup>2</sup>	Surface 100m <sup>2</sup>
Slag powder	Slag powder	Slag powder	Slag powder
0,4kg/m <sup>2</sup>	0,5kg/m <sup>2</sup>	0,6kg/m <sup>2</sup>	okg/m <sup>2</sup>
		11, 1,	

Fig.7. The experimental lot – a plowing area

Plots A1, A2 and A3 were added a quantity 0,4 kg/m<sup>2</sup>, 0,5 kg/m<sup>2</sup> respectively 0,6 kg/m<sup>2</sup> of slag powder. Plot A4 was used for comparison during the experiments, so it was not added any slag.

After the addition of slag, the adequate agricultural works were done (plowing, chisel plowing, seeding, fertilizing, mechanic and hand weeding). For the experimental plot, the culture of choice was maize.

During the experiments, we monitored the effect of slag addition upon the development of the plants. The results obtained two months after tilling and seeding are given in figure 8. One can notice the positive influence of slag addition upon the growing and blooming of the maize.



Fig.8. The experimental lot – a plowing area, after two months adding the slag



Fig.9. The experimental lot – a plowing area, after four months adding the slag

During the experiments, we monitored the effect of slag addition upon the development of the plants. The results obtained four months after tilling and seeding are given in figure 9. One can notice the positive influence of slag addition upon the growing and blooming of the maize.

#### Pilot researches – pasture

The experimental lot – pasture, was divided into four plots: P1-P4 shown in fig.10.

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P1		P2	P3	P4			
Surface 2	25m <sup>2</sup>	Surface 25m <sup>2</sup>	Surface 25m <sup>2</sup>	Surface 25m <sup>2</sup>			
Slag pov	vder	Slag powder	Slag powder	Slag powder			
0,4kg/	m <sup>2</sup>	0,5kg/m <sup>2</sup>	0,6kg/m <sup>2</sup>	0kg/m <sup>2</sup>			

# Fig.10. The experimental lot – pasture

The quantity of slag powder added to plots P1, P2 and P3 was 0,4 kg/m<sup>2</sup>, 0,5 kg/m<sup>2</sup> respectively 0,6 kg/m<sup>2</sup>. Plot A4 was used for comparison along the experiments, so it was not added any slag. The state of the pasture at the moment of adding the slag is shown in fig.11. The way in which slag powder addition influenced the development of the plants after two months is shown in fig.12. The way in which slag powder addition influenced the development of the plants after four months is shown in figure 13.









Fig.12. The experimental lot - pasture after two months adding the slag



Fig. 13 The experimental lot – pasture after four months adding the slag

The steel plant slag used in the experiments comes from the Martin steel plant, particularly in the smelting phase, a slag that is rich in CaO (35-46%) and P (0.2-0.9%). To the total content of iron in these slags, we should add crusts, splashings and other metallic inclusions, which, in virtue of the production flow, reach the slag taps and end up on the dump. Thus, one can notice that the total quantity of iron in a dump is practically equal with that in the slags existing in the furnace, but the amount of iron increases in the detriment of FeO and Fe2O3 as well as other components of the slag.

After processing, the total content of iron in the non-ferrous slag obtained is about 13,4% where FeO,  $Fe_2O_3$  and metallic iron are prevailing. The iron content of the non-ferrous slag is still quite high, as there are metal inclusions, missed by the metal separator, within the slag lumps. The other components of the non-ferrous slag have approximately the same level as in the non-processed slags. The non-ferrous steel plant slag (slag powder) has a basic character. It contains about 42% calcium oxide. This element is a lot more active from the chemical point of view, than any other lime additive. Added to the soil, it reduces its acid character and leads to its re-mineralization.

#### 4. CONCLUSIONS

The proposed technology does not generate other pollution sources and it is efficient from the economic point of view, it can be implemented in practice either by the producers of such wastes or by other firms using deferrized slag.

The use in other sectors of the steel shop slag leads to release the surfaces occupied by these wastes and to render them to the respective natural landscape, there takes place a reduction of the pollution degree in the regions having steel industry.

From this point of view, metallurgical slag processing aims, directly and indirectly, at two targets included in the community acquis: the control and reduction of soil pollution by



using clean technologies involving the turning of metallurgical slag wastes into recycled materials to be used in several domains: road and railway construction, hydro-technical and civil constructions, in the cement, glass and refractory materials industry, as well as in agriculture (improving soil acidity and re-mineralizing it).

Processing steel plant slags is beneficial for environment protection, community and agricultural welfare as well as from the technical point of view: metallurgical slags are nontoxic materials, with physical and chemical properties that are similar to rocks, so they represent a viable alternative, sometimes preferable to the natural variants for usage in constructions.

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# STUDIES REGARDING OF SIDERITIC RESIDUE UTILIZATION FOR CEMENT PRODUCTION

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#### Abstract:

The paper presents the experimentations made in the laboratories of Faculties of Engineering from Hunedoara and also in the frame of Carpatcement Holding Deva laboratories, looking at the introduction of the sideritic residue along with the clinker, for obtain of cement. For suggested recipe, were determinate the specific surfaces, setting time, compression strength. Result obtained in the laboratory condition proven as the proposal is viable as much from economic and ecologic point of view, through the recycling of manufactured residue existing in very big amounts in approach of Hunedoara area.

#### **Keywords:**

Sideritic residue, clinker production, cement, polluted surface, recycling.

## **1. INTRODUCTION**

The Portland cement is the most used binding material into construction, due to its properties, which are depending upon the chemical and mineralogical composition, manufacturing conditions etc. Portland cement has, normally, the following chemical composition:

CaO = 60 - 65%;  $SiO_2 = 18 - 24\%$ ;  $Al_2O_3 = 5 - 10\%$ ;  $Fe_2O_3 = 1 - 4\%$ ; MgO < 0.

From the point of view of the formal constituted elements, the chemical composition is presenting as follows:

 $\downarrow$  tricalcic silicate (3CaO·SiO<sub>2</sub>) symbolized C<sub>3</sub>S, in ratio of 47%;

- $\downarrow$  tricalcic silicate (2CaO·SiO<sub>2</sub>) symbolized C<sub>2</sub>S, in ratio of 28%;
- $\downarrow$  tricalcic aluminates (3CaOAl<sub>2</sub>O<sub>3</sub>) symbolized C<sub>3</sub>A, in ratio of 11%;
- 4 ferialuminat tricalcic (4CaO·Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>) symbolized C4AF, in ratio of 8%;
- 4 CaSO<sub>4</sub> (3%); MgO (2%); CaO<sub>liber</sub> (0,5%); Na<sub>2</sub>O (0,5%).[2]

The cement is obtained by raw material burning and smelting into the special installation: by dried, semi-dried, semi-wet and wet proceedings.

The raw material that is used for Portland cement manufacturing is composed by:

- calcareous rocs, with an calcite content of 75- 80%;
- 4 clay, with content of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>;
- adjustment adding, like: bauxite, for increasing Al<sub>2</sub>O<sub>3</sub> content; diatomite, for increasing SiO<sub>2</sub> content; ferric disulphide ashes, witch bring Fe<sub>2</sub>O<sub>3</sub> and decreasing temperature of clinkerization process; metallurgical slag, witch bring Fe<sub>2</sub>O<sub>3</sub>, thermo-central ashes and others wastes.

We are considering with a fundamental base technological solution of recycling the sideritic waste material, resulted on the cement producing.

## 2. THE STUDY

Aspects concerning the sideritic residue sludge beds are presented in figure 1.

The sideritic residue granulometric composition is presented in table 1. The simple granulometric curve is presented in figure 2 and the cumulate granulometric curves are presented in figure 3.





a.

b.



Figure 1. Aspects concerning the sideritic residue sludge beds c. a) sludge bed 1; b) sludge bed 2; c) sludge bed 3. Tab.1. The sideritic residue granulometric composition

Matorial		Granulometric classes, [µm]								
Material	< 25	25-56	56-90	90-180	180-315	315-500	> 500			
Sideritic residue	2,19	3,30	6,42	32,79	50,72	3,97	0,61			



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For experimentations, in order to obtained cement (fig.4), we elaborated 7 cement recipes, introducing various quantities of clinker and sideritic waste, as well as 5% burnt plaster (fig.5). The details are shown in tab.2 and graphically in fig.6.



Figure 4. Cement production flux.



Figure 5. The raw materials: clinker, sideritic waste, calcined gypsum.

Tab.2. The experimented cement recipes comp	onents

Component [0/]	Recipe no.								
Component, [%]	1	2	3	4	5	6	7		
Clinker	90	85	80	75	70	65	60		
Sideritic residue	5	10	15	20	25	30	35		
Calcined gypsum	5	5	5	5	5	5	5		
Total	100	100	100	100	100	100	100		

In order to determine the quality of our recipes we elaborated a 1 kg sample for each of them, according to the procedures shown in fig.7. We used in this scope the installations existing in the laboratories of our Faculty [3].







Figure 7. Cement technological flux in laboratory condition

## 3. ANALISES, DISCUSIONS, APPROACHES, INTERPRETATIONS

- The determination of quality has been done as follows:
- we performed the chemical analysis of the samples, the results being given in tab.3;
- we determined the specific surface of the cement mixture, tab.4;
- we carried out cement specific tests and determinations such as: the determination of water for the normal consistence paste, the binding time, resistance to pressure after 1, 2 and 7 days from binding – tab.5.

The tests have been done both in our laboratories and with the help and participation of our contract partner: CARPATCEMENT HOLDING, Deva branch. The chemical structure varied as shown in tab.3.

Recipe	Chemical composition, [%]									
no.	CaO	$SiO_2$	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	Others oxides	P.C.	CaSO <sub>4</sub> *0,5H <sub>2</sub> O			
1	60,53	20,78	5,00	3,64	3,97	1,17	4,90			
2	58,04	21,44	4,88	3,85	4,54	2,35	4,90			
3	55,54	22,10	4,75	4,06	5,12	3,52	4,90			
4	53,04	22,76	4,62	4,28	5,70	4,69	4,90			
5	50,54	23,42	4,50	4,49	6,28	5,87	4,90			
6	48,04	24,08	4,37	4,70	6,86	7,04	4,90			
7	45,55	24,74	4,24	4,91	7,44	8,21	4,90			

Tab.3. Chemical composition for our cement recipes



In order to determine the specific surface, we used the Blaine permeability meter shown in fig.8 – from the laboratories of CARPATCEMENT HOLDING, Deva branch. The data we obtained are given in tab.4 and in figure 9.

Figure 8. Permeabilimetrul Blaine - automat 1 - piston; 2 - celula de permeabilitate; 3 display; 4 - panou comandă



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The experiments meant to determine the amount of water in the normal consistency paste and of the binding start time have been done in the laboratories of the Faculty of Engineering of Hunedoara, using a Vicat apparatus, shown in fig.10. We mention that the determinations were done according to all the norms in force. The data we obtained are given in tab.6 and in figure 11.





Figure 10. Vicat apparatus for determination of water for the normal consistence paste and resulting proofs.

	Table. The quality characteristics for our cement recipes										
Charactoristics			Recipe no.								
Characteristics		1	2	3	4	5	6	7			
Water for the normal consistence paste, [cm <sup>3</sup> ]			74	73	65	67,5	67	66			
The binding time, [min]		16	19	14	13	15	18	18			
Resistance to pressure,	1 day	2,30	2,10	1,80	1,40	3,30	2,50	2,50			
	2 days	4,00	3,50	3,10	2,30	5,40	3,90	3,90			
	7 days	7,00	7,25	7,81	6,25	9,80	7,00	6,87			





Figure 11. The resistance to pressure variation of cement proofs



The resistance to compression has been tested by means of the device shown in fig.12, existing in the testing laboratories of CARPATCEMENT HOLDING Deva branch.

Figure 12. Compressing testing machine for cement sample 1 – machine bench; 2 – test specimen; 3 - panel.

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### 4. CONCLUSIONES

The resulting experimental data have lead to the following obvious conclusions:

- the resistance to pressure of the cement test samples, where part of the clinker has been replaced by siderite waste, is comparable to that of regular cements;
- the specific surface has a high influence upon the resistance to pressure and one can see that the larger the specific surface, the larger the resistance to pressure.
- the resistance to pressure of experimental cements increases with time, so that one can notice that, after 7 days, resistance is 3 times higher than the resistance determined after 1 day;
- the highest resistance to pressure after 7 days was obtained for recipe no. 5, to which we added 25% siderite waste;
- particular attention should be paid in further researches to the fine grinding of cement, so as to obtain a specific surface above 3000 cm<sup>2</sup>/g;
- the quantity of water for the normal consistency paste is smaller than the one usually recommended for cement: 70-90 cm<sup>3</sup>;
- the binding start time obtained in laboratory conditions recommends the use of experimental cements for road leveling layers, as they harden fast (with a higher addition of water).

At present, the acquisition price of cement is about 115 C/t, out of which 22 C/t represents the value of raw materials. The partial replacement of clinker by siderite waste leads to about 21% cut down on raw materials (the calculation referring to recipe 5, which has the best characteristics), respectively 4% of the price of cement.

Moreover, one has to consider the ecological impact, resulted from the removal of the waste ponds.

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# **RESEARCHES CONCERNING TO THE POSSIBILITY OF USE THE SIDERITIC RESIDUE FOR PRODUCTION OF CLINKER**

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#### Abstract:

The work presents some researches regarding to utililisation in cement industry of the sideritic residue, stored in the ponds near from Hunedoara. Thus, on the chemical and granulometric compositions is obtained a number of 10 recipes of clinker, and finally are presented an optimum recipe. The purpose of this researches was reused a manufactured residue, which momentary is stored on large ground surfaces. Through suggested variant are desired the rendition to natural area of this polluted surfaces, parallel with economic effect for reducing quantities of calcite and clay in clinkers production from the cement industry.

#### **Keywords**:

Sideritic residue, clinker production, cement, polluted surface, recycling

## **1.INTRODUCTION**

The metallurgical industry represents a strong source of environment pollution related through the amounts of gas and dust emanates in atmosphere and the through residues quantities stored in ponds on dumps.

In this the sense the iron ore the type siderite with ferric contents of 25-40% and roasted in the sight of carbon oxide eliminate, what causes concentration of iron ore and transformation of mineral from carbonate in iron oxide with magnetic property. Behind of magnetic concentration operations, in result concentrate the iron arrives at concentration of 51-53%, can be used in agglomeration process, and sterile is stored in ponds.

Suchlike this technological process it was at ore preparation plan of Teliuc- Hunedoara, within 1998 when the primary elaboration steel flux (coke plant - Siemens-Martin steelwork) from S.C. Siderurgica S.A it was complete deallocated.

In afferent ponds ore preparation plan of Teliuc- Hunedoara it was remained stored in ponds huge quantities of siderite sterile (cca 12 mil. tons)

Sterile can be submitted to a concentration operations, and resulted sterile (secondary sterile) can be used-up as the correction addition for obtains of clinker (the chemical composition permits this thing).

### 2. THE STUDY

In order to be determined the quantities of the waste materials deposited into the ponds within Hunedoara aria the topographic measurements have been performed in the system of 1970's stereographic coordinates and for reference system of Black Sea quotes. In the fig. 1 it is presenting the design of framing in the aria of the studied emplacements. The fig.2 presents the framing design in the aria of 1 Pond, respectively the fig. 3 for the 2-nd and the 3-rd Ponds [3].

The data obtained by measurements were worked in AUTOCAD adding program resulting the situational plans from which is caused the amounts of existing residues.

Analyzing the measurements and situational plans obtained for the objective taken under consideration results the next amounts of stored residues:



- Sludge bed no.1 Teliuc excavation: the sludge bed deals a surface of 25 hectare, the amount of residues (sideritic concentrate) 7 million tons.
- Sludge bed no.2 Teliuc excavation: the sludge bed deals a surface of 18 hectare, the amount of residues (sideritic concentrate) 5 million tons.
- Sludge bed no.3 Teliuc excavation: the sludge bed deals a surface of 32 hectare, the amount of residues (sideritic concentrate) 9 million tons.



Figure 1. The integration plan in studious emplacement zone.



Figure 2. The integration plan in sludge bed no.1 Teliuc area.





Figure 3. The integration plan in sludge bed no.2 and 3, Teliuc area

The sideritic residue chemical composition (the 10 proofs taken and average value) is presented in table 1 and the chart, in figure 4.



Figure 4. Taken samples chemical composition

Table 1. The succide residue chemical composition from studge beds, [%]									
The sideritic residue from sludge beds	CaO	SiO <sub>2</sub>	$Al_2O_3$	$Fe_2O_3$	Others component	P.C.			
1	16,54	35,02	2,84	7,8	14,98	22,82			
2	16,27	34,8	3,04	7,94	15,22	22,73			
3	16,59	34,91	3	8,04	15,46	22			
4	16,55	33,89	2,68	7,8	15,01	24,07			
5	16,48	34,22	3,07	7,9	14,63	23,7			
6	16,34	34,25	2,88	7,54	14,75	24,24			
7	16,44	34,28	2,75	7,85	15,21	23,47			
8	16,4	34,19	2,81	8,01	14,95	23,64			
9	16,22	34,1	2,85	7,88	15,15	23,8			
10	16,07	34,24	2,78	7,64	15,04	24,23			
Average	16,39	34,39	2,87	7,84	15,04	23,47			

We experimented a number of 10 recipes with component presented in table 2; the chemical composition of the recipes with and without the loss to calcinations it presented in figure 5 and 6 [3].



Component		Recipe no.								
Component	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
Calcite	72	72	75	73	74	74	75	75	76	76
Clay	14	15	13	14	13	14	12	13	12	13
Sideritic residue	14	13	12	13	13	12	13	12	12	11
Total	100	100	100	100	100	100	100	100	100	100







Figure 6. Chemicals composition of recipes without losses by calcinations



The raw materials was worked, base of the technological flux presented in fig. 7. The crushing (the clay and the limestone came in bunches), we used a ball mill, existing the Metallic Smelting Laboratory. After crushing (the resulting grain size being below  $250\mu$ m), the materials were graded in the laboratory installation, dosed, by

Figure 7. The raw materials worked technological flux in order to obtained clinker

means of analytical scales and homogenized in a homogenizing drum. Fig. 8 shows aspects of these experiments.



Figure 8. The installations used for clinker production



After the recipes have been obtained, the materials were clinkerized in a Tamman resistance furnace, each sample weighing 200g. The resulting samples showed a degree of reduction ranging between 30-42,5%.

#### 3. ANALISES, DISCUSIONS, APPROACHES, INTERPRETATIONS

The Portland clinker represents the product obtained by calcinations till to the partial smelting, of a homogenous mixture, fine crushing, of the calcareous and as clay raw materials, and, eventually, different for correction additions. In the technology of the Portland cement manufacturing, the clinker represents a semi-finished product.

The clinker chemical composition of Portland cement represents the percentage content shown in the chemical elements, computed as oxides. The chemical composition is expressed in oxides because the chemical transformations ,which the raw materials are suffering during the clinkering, do not involve the destruction of the liaisons between the respective elements and Oxygen, so, in the new formed constituted elements, the oxides are coming into as the molar well constituted units.

The clinker characterization, from the oxides composition point of view, can be made using the **modules**. The modular system is based on the co-relations that are established between the oxidic composition and mineralogical one, of the clinkers, simplifying by this the computation of the gross mixture and deduction of some characteristics of the cements will follow to be manufactured [1]. The main modules used in there cement industry are: the module of silica, module of alumina and grade of saturation in calce.

*The module of silica* ( $M_{Si}$ ) represents the ration between the percentage content of SiO<sub>2</sub> and percentage content of  $Al_2O_3$ +Fe<sub>2</sub>O<sub>3</sub> from the clinker.

$$M_{Si} = \frac{\% SiO_2}{\% AI_2 O_3 + \% Fe_2 O_3}$$
(1)

The clinkers of Portland cement have, normally,  $M_{Si}=1,5...4$ . The silica module value is given the information regarding mineralogical composition of the clinker, respectively upon the content of silicates and aluminates:  $(C_3S+C_2S)/(C_3A+C_4AF)$ , as well as upon the conduct of the gross mixture on burning, regarding the content into the liquid phase (the silicates remained into the solid phase, and in the meantime aluminates, merely ferrite-aluminates passed into the liquid phase). In case of a high module of silica, the clinkering is realized in more difficult conditions; for the values of silica module higher than 2.5 the clinkering is made harder, with a great consumption of energy; for  $M_{Si} = 2...2,5$  the clinkering is going normally, and for  $M_{Si}$  lower than 2, the clinkering is making easy. The clinkers with  $M_{Si}$  lower than 1,5 give the cements with very speedy connection/bind.

*The module of alumina* ( $M_{Al}$ ) is the ration between the percentage content of  $Al_2O_3$  and  $Fe_2O_3$  of the clinker:

$$M_{AI} = \frac{\% AI_2 O_3}{\% Fe_2 O_3}$$
(2)

For the common clinkers, the module of alumina has the values comprised between 0.2 and 5. Its value gives the information regarding the percentage of aluminates phases. Ferrite and ferrite-aluminates phases from the clinker:

- **a**t  $M_{Al}$  higher than 0.64, all quantity of  $Fe_2O_3$  appears as binded in ferrite-aluminate solid solution, the over plus of de  $Al_2O_3$  is forming  $C_3A$ ;
- **↓** la  $M_{Al}$  lower than 0.64, all quantity of  $Al_2O_3$  appears as binded in ferrite-aluminate solid solution, the over plus of Fe<sub>2</sub>O<sub>3</sub> is forming C<sub>2</sub>F;
- 4 M<sub>Al</sub>=0.64, all quantity of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> is binded with CaO as C<sub>4</sub>AF [2].

The degree of saturation in calce  $(S_K)$  represents the ration between the percentage content of CaO that exists in the clinker and the quantity of CaO that is necessary for the saturation of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> at the mineralogical constituted elements that are characteristically to the clinker, with the condition that CaO to not remain un-binded (free):

$$S_{K} = \frac{\% CaO}{2,8\% SiO_{2} + 1,1\% AI_{2}O_{3} + 0,7\% Fe_{2}O_{3}}$$
(3)



Tuble 5. offices enclinear composition of tax materials								
Paw	Oxides chemical composition of raw materials, [%]							
materials	CaO	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	Others oxides	Losses by calcinations		
Calcite	53,2	3,0	1,5	1,0	0,5	41,8		
Clay	5,51	52,56	13,21	6,32	7,44	14,96		
Sideritic residue	16,39	34,3 9	2,87	7,84	15,04	23,47		

Table 3. Oxides chemical composition of raw materials

The standard calce ( $K_S$ ) is used to us, also, that coincides with the formulation given by German scholarly Kühl for the saturation grade in calce, but the value  $S_K$  will be multiply with 100.

In order to obtain in the laboratory a clinker of the cement there were used as the raw materials the calcareous stone and clay from CARPATCEMENT HOLDING – Deva factory and sideritic waste material from Teliuc pond. The chemical composition of these raw

Table 4. Blends of raw materials for clinker produ	uction
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No.	Blend c	omposi	Modular compositions		
proof	Calcite	Clay	Sideritic residue	Sĸ	$\mathbf{M}_{\mathrm{Si}}$
1	72	14	14	0,905	2,376
2	72	15	13	0,893	2,371
3	75	13	12	1,012	2,318
4	73	14	13	0,932	2,355
5	74	13	13	0,98	2,34
6	74	14	12	0,961	2,335
7	75	12	13	1,025	2,322
8	75	13	12	1,008	2,318
9	76	12	12	1,058	2,300
10	76	13	11	1,04	2,296

materials is given in the table 3.

Based on the composition of the clinker obtained CARPATCEMENT at HOLDING SA -Deva Factory, the computations have been done for the determination of the percentage composition of the gross mixture formed by calcareous stone, clay and sideritic waste material and which from must result a clinker that will follow to have  $S_{K}=0.98$  and  $M_{Si}$  = 2.34. We made modular calculus for all blends of raw matters; the results are presented in table 4.

# 4. CONCLUSIONES

There can be observed that the optimum mixture is from the **sample 5**, because at the samples 3, 7, 8, 9 and 10 (to which the percentage of calcareous stone is more than 74%), the grade of saturation in calce has a value higher than 1, and it means that from the mixture of the raw materials, after clinkering, will remain free CaO that is damaging the quality of the clinker. At the samples 1, 2, 4, and 6, the value of the saturation grade into the calce is lower than that one of the clinker we like to obtain.

Referring to the values of the silica module, there can be observed that they do not present significant variations for the samples are analyzed.

So, in order to obtain an adequate clinker, the blend of raw matters must content the follow: 74 % calcite; 13% clay; 13 % sideritic residue.

The analysis of the results has lead to the following conclusions:

- the process has a low economical efficiency, as this solution requires a further clinkering process and replaces only partially some quantities of clay and limestone by sideritic waste;
- considering the actual economical context, we are looking for solutions meant to reduce the amount of clinker used in cement production, which have direct implications on its cost, and which also have a positive ecological impact;
- the aspect of the lab samples shows that there is a large quantity of vitreous mass surrounding the alite and belite crystals, which determines the clinker hydrating process to slow down and a reduction of the mechanical strength of the resulting hardened cement.

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# THE IMPORTANCE OF NON-CONVENTIONAL BIOFUEL UTILIZATION FOR POLLUANT EMISSIONS REDUCTION

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#### Abstract

In this paper are presented aspects concerning biofuels utilization as a result of traditional fuels disadvantages. Global depletion of oil resources and global warming has caused the occurrence and development of biofuels market although the production of energetic plants competes with crops for food products. Combining the benefits of economic, environmental and energy security resulting from the utilization of biofuels, attracts the interest and support of the population, but also of many governments, and the result will probably be the increase of biofuels utilization.

#### Key words:

biofuel, emissions, greenhouse effect, energetic plants, transport

### **1. INTRODUCTION**

The reducing of global recoverable reserves of fossil hydrocarbons and successive increase of the oil barrel price, as a result of the oil crisis, have created favourable premises to approach other sources for obtaining fuels. The restrictive legislation on the environmental pollution caused by the combustion gases of conventional fuels also contributes to finding alternative energy sources. So, there are concerns for the production of biofuels from renewable feed stocks (biomass).

The fossils resources are worldwide distributed and quantitative limited while the annual consumption is growing. Analyzing the distribution of the world of crude oil reserves, an alarming situation has been discovered in some areas which are big petroleum derivatives consumers, such as Western Europe [5].

Oxides of nitrogen and sulphur, smoke and incompletely burned hydrocarbons from exhausted gases of engines using classic fuels, are major pollutants of the atmosphere. The accumulation in the atmosphere of carbon dioxide resulting from classic fuels combustion, also contributes to enhance the greenhouse effect. Therefore, is necessary to obtain alternative fuels, as by their combustion to reduce considerably the quantity of pollutants emissions exhausted into the atmosphere and by using resources from renewable raw materials to eliminate the greenhouse effect due to an accumulation of carbon dioxide in the atmosphere.

One of the most recognized and consumed biofuels is the biodiesel, which is a fuel of plant origin obtained from rape oil, sunflower, soy, palm, or of animal origin obtained from burned and UFO materials (animal scraps, fat, hair, etc.)

Biofuel represents any fuel with 80% minimum content of materials derived from living organisms harvested no more than 10 years before producing that fuel. [3].

### 2. THE BENEFITS OF BIODIESEL

## **2.1. EFFICIENCY OF BIOFUEL PRODUCTION**

The market of classics fuel is one of the reasons for switching to biofuels. Great American auto manufacturers are already working on series engines with biofuels operation, and some European states are giving substantial subsidies to producers and importers of ethanol, a biofuel made mostly from corn.



Theoretically, any plant can be used for the production of biofuels. Practically, are preferred - from obvious economic reasons - plants that have a high content of oil or rich in starch. Americans, for example, are intensively cultivating mostly corn and soybeans; EU uses rape crops, and exotic countries as Brazil and the whole South-East Asia exploits at full the production of cane sugar and palm (palm oil is one of the cheapest raw materials for biofuel).

At present, the most efficient biofuel is produced from sugar cane or palm oil, therefore coming from the least developed countries in Africa, Asia and South America. Taxes imposed by certain powers to the biofuel import are excessive, making the profits of producers to be minimal, although they gave up on basic agriculture land for biomass crops. [5].

Biodiesel fuel is the first and only alternative fuel which has a full evaluation of the emissions produced by its combustion in internal combustion engines. The U.S. Environmental Pollution Agency (EPA) has evaluated in the "clean air" section, the effects on health caused by burning of diesel biofuel. Thereby, in the last 2 years were developed a series of programs related to the most stringent testing protocols required by EPA for certification of fuels and / or additives.

Many countries have a competitive advantage in producing biofuels. Meanwhile, many other countries are unable to meet their biofuel needs from domestic sources (Fig. 1).



Source: New Energy Finance www.newenergyfinance.com

Fig.1 Biofuel demands and production capacities for selected world regions

Also, when bioenergy displaces fossil fuels, in transport and power generation, or is produced in conjunction with soil carbon storage in the form of bio-char for example, opportunities arise for trade in carbon emission reduction units. [2]

Benefits of biodiesel:

- The potential for altering the ozone layer by forming "smog" is 50% lower for diesel biofuel (B100 and B20) than conventional diesel fuel due to nitrate polycyclic aromatic hydrocarbons reduction.
- Emissions of sulphur are completely eliminated by using B100. Exhaust gases pollutant 4 emissions no longer contain sulphuric oxides and sulphates (important components of acid rains), because in the molecular structure sulphur cannot be found in the case of B100 compared to the diesel one.
- Criteria for emissions estimations present a strong reduction of their values compared with conventional diesel fuel.
- Diesel biofuel reduce the disease risks that are usually caused by diesel. The emissions produced by biodiesel show the HCAP and nitrate-nHCAP reduction, both responsible for cancer [3], [1].



### 2.2. REDUCING EMISSIONS AND THE GREENHOUSE EFFECT OF USING BIOFUEL

Biodiesel - an ultra-clean fuel - contains no sulphur or aromatics, which contributes to emissions reduction.

Biofuel is used mainly as a source of reduction pollution caused by cars. It is well known the fact that the largest source of greenhouse gases is the transport. Used as fuel, biofuel reduces oxides of nitrogen, monoxide and carbon dioxide pollution.

Transport and fuel production are responsible for one quarter of gas emissions with greenhouse effect, and the percentage is continuously increasing.

"Energy crops" for biofuels have the potential to decrease by over 10% the emissions of greenhouse gases (compared to gasoline and diesel) because such cultures retain the carbon in the ground as they grow. [4]

For example in Ireland, emissions of the different gases can be aggregated on the basis of their Global Warming Potentials which are a measure of their relative warming effect. The relative contributions of the different gases are shown in Figure 2.



Fig.2 Contribution of different greenhouse gases to aggregate emission

The contribution of methane and nitrous oxide to total emissions is unusually high compared to that in other developed countries. This is because of the significance of agriculture in the economy; agricultural emissions represent 35% of total emissions. [6]

The development of biofuel industry in Romania provided an explosive progress in agriculture: in 2005 rape crops covered 88,000 hectares. In 2006, the area has reached to 160,000, and in the autumn of last year 370,000 hectares were sown with rape.

EU Commission White Book acknowledges that by 2010 the  $CO_2$  emissions will reach a significant increase, their amount being of approximately 1113 million tones. The major responsible is the road traffic which causes from transports 84% of total  $CO_2$  emissions. Therefore, from ecological point of view the White Book campaigns to reduce the oil dependence in transports (which is currently approximately 98%) by using alternative fuels such as biofuels. Using biofuels on a large-scale in transports constitutes only a part of the package of measures to be taken to achieve the reduction in  $CO_2$  emissions. The increase of biofuels utilisation in the transport sector, without excluding other possible alternative fuels for the automotive industry, is one of the ways through which the dependence on energy imports can be reduced, can be influenced the fuel market for transports and can be ensured the security of energy supply on medium and long term.

# 4. CONCLUSIONS

The gradual transition from fossil fuels to biofuels involves both compromises and many risks, besides benefits and opportunities, under the circumstances of which there already exists a young but rapidly growing market. Simultaneously the political and economic interests around biofuels are immense. The mode of producing and using the alternative energy makes the difference.



Even if Romania has resources of fossil hydrocarbons, the production and utilisation of biofuels has a great importance, both in the national and in European context.

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# RESEARCH ON THE RELIABILITY MODELING OF HYDRO MECHANICAL SYSTEMS

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### **Abstract:**

The paper presents reliability evaluation models of the pumping system for slag and ashes discharge, from thermo-electric power plants (TPP). The paper it is structured in four parts. The first two parts present the system reliability modelling using the Markov model, respectively binomial model. The time and outflow availability modelling of analyzed system are represented in the third part. The last part presents the conclusions. In order to facilitate the understanding of the models it has been concretized with reference to the slag and ashes exhausting system from CET I Oradea, equipped with Bagger pumps.

#### **Keywords**:

hydro mechanical systems, reliability modeling, Markov model, binomial model, time and outflow availability.

# **1. INTRODUCTION**

Usually, the slag and ashes which result from coal burning, are evacuated using the Bagger pumps. For thermo-electric power plants it has been established that the slag and ashes continuous evacuation directly conditioning the cauldron working. Therefore, the number of Bagger pumps establishment and their drive back connections, represent the subject for the technical and economic reliability and optimization calculus.

The reliability modeling, it has been made for the functioning configuration in which the Bagger pumps stations (BgPS) are "n+k" systems (n in work, k in reserve). For forecasting reliability analyzing the most used methods are [1, 2, 5, 6]:

- the binomial method, where the elements are characterized by states probabilities (p,q);
- the Markov method with continuous parameter, where the elements are characterized by fundamental reliability indicators (λ<sub>i</sub>, μ<sub>i</sub>).

## 2. THE MARKOV METHOD USED TO RELIABILITY MODELLING OF SLAG AND ASHES PUMPING SYSTEM FROM CET I ORADEA

There are three Bagger pumps stations provided foe slag and ashes exhausting in CET I Oradea:

- the Bagger station 1: attends the 1, 2 and 3 cauldrons and it is equipped with 5 Bagger pumps;
- the Bagger station 2: attends the 4 and 5 cauldrons and it is equipped with 4 Bagger pumps;
- the Bagger station 3: attends the cauldron 6 and it is equipped with 3 Bagger pumps.

The continuous and safety functioning of Bagger pumps it is very important for continuous and nominal output functioning cauldrons.

For Bagger pumps dimensioning like "n+k" systems, the forecasting reliability indicators calculus are following presented.

a). The Bagger station I has 5 Bagger pumps, SIGMA 250-NBA-580 type and an outflow of Q = 800 m<sup>3</sup>/h. Functioning configurations is "3+2" (3 in work and 2 in reserve). Because the groups are identical it has been admitted the same values for reliability indicators. The total number states of a system with 5 elements are  $2^{5}=32$ . In this case

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(identical elements) states are merged and RED (reliability equivalent diagram) is represented in figure [2, 3]:



The states graph is presented in figure 2:



Figure2. The states graph of "3+2" system

**4** The transition intensities matrix [q<sub>ij</sub>] has the 6<sup>th</sup> rank and it is [1, 2, 3, 5, 6]:

	1	2	3	4	5	6	
1	-5λ	μ	-	-	-	-	
2	5λ	$-\mu - 4\lambda$	2μ	-	-	-	
3	-	4λ	$-2\mu-3\lambda$	3μ	-	-	(
4	-	-	3λ	$- \ 3\mu - 2\lambda$	4μ	-	
5	-	-	-	2λ	$-\;4\mu-\lambda$	5μ	
6	-	-	-	-	λ	– 5µ	

**4** The equations system:

$$\begin{cases} -5\lambda p_{1} + \mu p_{2} = 0\\ 5\lambda p_{1} - (\mu + 4\lambda)p_{2} + 2\mu p_{3} = 0\\ 4\lambda p_{2} - (2\mu + 3\lambda)p_{3} + 3\mu p_{4} = 0\\ 3\lambda p_{3} - (3\mu + 2\lambda)p_{4} + 4\mu p_{5} = 0\\ 2\lambda p_{4} - (4\mu + \lambda)p_{5} + 5\mu p_{6} = 0\\ \lambda p_{5} - 5\mu p_{6} = 0\\ \sum_{i=1}^{6} p_{i} = 1 \end{cases}$$

$$(2)$$

The system solution leads to probability vector determination  $[p_i]$ ,  $i=1\div 6$  with which the reliability indicators are calculated.

Similarly the other Bagger pumps stations from slag and ashes exhausting system will be analyzed and the numerical data will be tabular represented.

b) The Bagger station 2 has 4 Bagger pumps, SIGMA 250-NBA-580 type and an outflow of Q = 800 m<sup>3</sup>/h. Functioning configuration is "2+2" (2 in work, 2 in reserve).
↓ The states graph is presented in figure 3:





**4** The equations system:

$$\begin{cases} -4\lambda p_{1} + \mu p_{2} = 0 \\ 4\lambda p_{1} - (\mu + 3\lambda)p_{2} + 2\mu p_{3} = 0 \\ 3\lambda p_{2} - (2\mu + 2\lambda)p_{3} + 3\mu p_{4} = 0 \\ 2\lambda p_{3} - (3\mu + \lambda)p_{4} + 4\mu p_{5} = 0 \\ \lambda p_{4} - 4\mu p_{5} = 0 \\ \sum_{i=1}^{5} p_{i} = 1 \end{cases}$$
(3)

The system solution leads to probability vector determination  $[p_i]$ ,  $i=1\div 5$  with which the reliability indicators are calculated.

c) The Bagger station 3 has 3 Bagger pumps, SIGMA 250-NBA-580 type and an outflow of Q = 800 m<sup>3</sup>/h. Functioning configuration is"1+2" (1 in work, 2 in reserve).
 ♣ The states graph is presented in figure 4:



Figure 4. The states graph of "1+2" system

4 The equations system:

$$\begin{cases} -3\lambda p_{1} + \mu p_{2} = 0\\ 3\lambda p_{1} - (\mu + 2\lambda)p_{2} + 2\mu p_{3} = 0\\ 2\lambda p_{2} - (2\mu + \lambda)p_{3} + 3\mu p_{4} = 0\\ \lambda p_{3} - 3\mu p_{4} = 0 \end{cases}$$
(4)  
$$\begin{cases} 4\\ \sum_{i=1}^{4} p_{i} = 1\\ \sum_{i=1}^{4} p_{i} = 1 \end{cases}$$

The system solution leads to probability vector determination  $[p_i]$ ,  $i=1\div4$  with which the reliability indicators are calculated.

The states grouping for each one of the pumping stations is done in the following way:

$$BgPS 1 \begin{cases} S = [S_1, S_2, S_3] \\ R = [S_4, S_5, S_6] \end{cases}$$
$$BgPS 2 \begin{cases} S = [S_1, S_2, S_3] \\ R = [S_4, S_5] \end{cases}$$
$$BgPS 3 \begin{cases} S = [S_1, S_2, S_3] \\ R = [S_4] \end{cases}$$

The calculus expressions of reliability indicators for the Bagger pumps stations are represented in table 1.

The reliability indicators	Bagger pumps stations				
The reliability indicators	BgPS 1	BgPS 2	BgPS 3		
0	1	2	3		
Ps	$\sum_{i=1}^{3} p_i$	$\sum_{i=1}^{3} p_i$	$\sum_{i=1}^{3} p_i$		
P <sub>R</sub>	$\sum_{i=4}^{6} p_i$	$\sum_{i=4}^{5} p_i$	p <sub>4</sub>		

 Table 1. The calculus of states probabilities and reliability indicators for the Bagger pumps stations

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Table 1 (continuation	)
-----------------------	---

0	1	2	3
$\alpha(T_A)$	$\sum_{i=1}^{3} p_i \cdot T_A$	$\sum_{i=1}^{3} p_i \cdot T_A$	$\sum_{i=1}^{3} p_i \cdot T_A$
$\beta(T_A)$	$\sum_{i=4}^{6} p_i \cdot T_A$	$\sum_{i=4}^5 p_i \cdot T_A$	$p_4 \cdot T_A$
$\nu(T_A)$	3p <sub>3</sub> λT <sub>A</sub>	2p <sub>3</sub> λΤ <sub>Α</sub>	$p_3 \lambda T_A$
MTBF	$\frac{3}{\sum_{i=1}^{3} p_i} / 3 p_3 \lambda$	$\sum_{i=1}^{3} p_i / 2p_3 \lambda$	$\frac{\sum_{i=1}^{3} p_{i}}{p_{3}\lambda}$
MTM	$\sum_{i=4}^{6} p_i / 3p_3 \lambda$	$\sum_{i=4}^{5} p_i / 2p_3 \lambda$	$p_4/p_3\lambda$
$\lambda_{ m s}$	$3p_3\lambda / \sum_{i=1}^3 p_i$	$2p_3\lambda / \sum_{i=1}^3 p_i$	$p_3\lambda / \sum_{i=1}^3 p_i$
μ <sub>s</sub>	$3p_3\lambda / \sum_{i=4}^6 p_i$	$2p_3\lambda / \sum_{i=4}^5 p_i$	$p_3\lambda/p_4$

Admitting the values of Bagger pumps fault mean rate, respectively recovery mean rate from [7]:  $\lambda_{BgP} = 40 \cdot 10^{-4} h^{-1}$ ;  $\mu_{BgP} = 119 \cdot 10^{-4} h^{-1}$  the following results in table 2 had been obtained.

Table 2. Numerical values of reliability indicators for Bagger pumps stations

The reliability	Bagger pumps stations							
indicators	BgPS 1	BgPS 2	BgPS 3					
0	1	2	3					
Ps	0,8934395	0,9485405	0,9840781					
P <sub>R</sub>	0,1065605	0,0514595	0,0159216					
$\alpha(T_A)[h]$	7826,53	8309,2148	8620,5242					
$\beta(T_A)[h]$	933,46998	450,78522	139,47322					
ν(T <sub>A</sub> ) [faults per year]	27,8477	9,958424	4,979212					
MTBF [h]	281,04692	834,39054	1731,3029					
MTM [h]	33,520457	45,266723	28,011103					
$\lambda_{s}[h^{-1}]$	$3,5581158 \cdot 10^{-3}$	1,1984796·10 <sup>-3</sup>	5,7759968·10 <sup>-4</sup>					
μ <sub>s</sub> [h-1]	0,0298325	0,0220912	0,0357001					

### 3. FORECASTING RELIABILITY EVALUATION OF BgPS USING BINOMIAL METHOD

The binomial method appeals to an easier mathematical model than the Markov method.

In this case for reliability indicators evaluation, we must start from the binomial theorem expression. For "n+k" BgPS type is:

$$(p+q)^{n+k} \tag{5}$$

The reliability indicators evaluation has been made by the following relations: The time safety of system with "n" groups in work (successfully probability) is:

$$P_{S} = \sum_{i=n}^{n+k} C_{n+k}^{i} \cdot p^{i} (1-p)^{n+k-i}$$
(6)



↓ The time safety of BgPS with "n+k-j" groups in work is:

$$P_{n+k-j} = \sum_{i=n}^{n+k-j} C_{n+k-j}^{i} \cdot p^{i} (1-p)^{n+k-j-i} cu j \le k$$
(7)

The feasible states of BgPS I are presented in table 3 and 4. The functioning probability, respectively the failure probability for Bagger pumps, including the electrical equipment are [7],  $p_{BgP}=0,748$ ;  $q_{BgP}=0,252$ .

	Table 3. The feasible states of BgPS 1									
Analytical processing										
State pr	E	BgP sta	te	State Annual mean		Achieved mean				
State III.	f	rs	d	probability	time [h/an]	outflow [m <sup>3</sup> /h]				
1(s)	3	2	-	р <sup>5</sup>	р <sup>5</sup> · Т <sub>А</sub>	$3Q_{BgP}$				
2(s)	3	1	1	5p <sup>4</sup> q	5p <sup>4</sup> q∙T <sub>A</sub>	$3Q_{BgP}$				
3(s)	3	I	2	10p <sup>3</sup> q <sup>2</sup>	10p <sup>3</sup> q <sup>2</sup> · T <sub>A</sub>	$3Q_{BgP}$				
4(sp)	2	-	3	10p <sup>2</sup> q <sup>3</sup>	10p <sup>2</sup> q <sup>3</sup> · T <sub>A</sub>	$2Q_{BgP}$				
5(sr)	1	-	4	5pq <sup>4</sup>	5pq <sup>4</sup> · T <sub>A</sub>	1Q <sub>BgP</sub>				
6(r)	-	-	5	q <sup>5</sup>	$q^5 \cdot T_A$	-				
	т	ablad	NTerror		$\mathbf{L} = \mathbf{D} \cdot \mathbf{D} \mathbf{C} \cdot $	1.1				

Table 4. Numerical values of the BgPS 1 feasible states

Numerical results for BgPS I									
State nr.	H	3gP sta	te	State	Annual mean	Achieved mean			
	f	rs	d	probability	time [h/an]	outflow [m <sup>3</sup> /h]			
1(s)	3	2	-	0,2341574	2226	2400			
2(S)	3	1	1	0,3944363	3455	2400			
3(s)	3	-	2	0,2657699	2328	2400			
4(sp)	2	-	3	0.0895374	784	1600			
5(sr)	1	-	4	0,0150825	132	800			
6(r)	-	-	5	1,01625·10 <sup>-3</sup>	9	0			

rs – the reserve state; sp – the partial success (66,6 %); sr – the reduced success (33,3 %) Q<sub>BgP</sub> – the pump outflow

The successfully probabilities expressions for the other pumping systems are given in table 5. The reliability indicators calculus are made according to the previous models. Table 5. Numerical values of successfully probability for pumping systems

	Tuble J. Humerlear values of successfully probability for pullping systems									
	Bagger	Cont	figuration	The indicator P <sub>s</sub>	Numerical					
Nr.	station	Established	Normal functioning	relation	results for $P_S$					
1.	SPBg 2	4xSIGMA	2+2	$p^4 + 4p^3q + 6p^2q^2$	0,9480862					
2.	SPBg 3	3xSIGMA	1+2	$p^3 + 3p^2q + 3pq^2$	0,9839969					

Corroborating with groups outflow the availability indicators of BgSP can be calculated: • The successfully probability is:

$$P_{\rm S} = p^5 + 5p^4q + 10p^3q^2 = 0,8943636 \tag{8}$$

• The failure probability is:

$$P_{R} = 20p^{2}q^{3} + 5pq^{4} + q^{5} = 0,1056364$$
(9)

• The medium number of functioning groups, respectively the failures groups:  $m_f = 5p \approx 4$ ;  $m_d = 5q \approx 1$  (10)

$$f = 5p \cong 4; m_d = 5q \cong 1$$
 (10)

 $\bullet$  The standard deviation in comparison with the mean value (m<sub>f</sub>):

$$=\sqrt{5pq} = 0,94248$$
 (11)

• The pumping volume during the analysis interval:

σ



$$V_{p} = \sum_{i=1}^{5} Q_{i} \cdot T_{i} = 20 \cdot 10^{6} \text{ m}^{3} / \text{an}$$
(13)

• The unavailable volume during the analysis interval:

$$\Delta V_{I} = V_{N} - V_{p} = 4 \cdot Q_{PBg} \cdot T_{A} - V_{p} = 8 \cdot 10^{6} \text{m}^{3} / \text{an}$$
(14)

• The availability and unavailability indicators:

$$D_{Q} = \frac{V_{p}}{V_{N}} = 0,7134703$$
(15)  
$$I_{Q} = 1 - D_{Q} = 0,2865298$$

### 4. CONCLUSIONS

**1.** In reference material one cannot find a specific treating (dedicated, adequate, distinct and profound) of BgPS forecasting reliability;

- 2. For Bagger pumps system reliability evaluation the following models are recommended:
  - the Markov model for "n+k" system ("3+2", "2+2", "1+2"),
    - **4** the binomial model "n+k";
    - the outflow availability and unavailability evaluation, using the binomial;

**3.** With reference to the numerical results obtained for CET I Oradea BgPS it has been ascertained a better behavior of Bagger station 3, from the reliability point of view.

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# **FUZZY SIMULATION IN RELIABILITY ANALYSIS**

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#### Abstract:

In the first part of this paper we present an introduction of fuzzy logic application in power systems and equipments reliability analysis. The second part considers the development of a computer simulation program for complex electric system's reliability study fuzzy algorithms, definition of asymmetric Gauss input and output membership functions, rule sets and results display methods. The third part is focused on the development of a case study for the electric station in Tileagd, Bihor County using the developed simulation program in the Matlab environment. The fourth part emphasis on the conclusions which show the importance and efficiency of fuzzy modeling in reliability analysis by comparative evaluation of fuzzy and Monte Carlo methods also shown in equivalent reliability diagrams, highlighting authors contributions. The last part of the paper presents the references which were consulted.

**Keywords:** failure tree, reliability, fuzzy simulation

## **1. INTRODUCTION**

Fuzzy logic represents an extremely useful tool in modeling the behavior of electrical equipment. Fuzzy set theory considers multi state systems and multi criteria decisions, the mathematical instrument is flexible and easily adaptable to reality. This theory is useful for modeling of power systems and equipment reliability evaluation [1, 9].

In reliability studies it is generally accepted a bivalent operational evolution mode: normal operation state and failure state. In reality the transition between states is not sudden, which implies a nuanced expression of system's performance (very good, good,..., median, poor). In this paper there is presented the development of reliability simulation software for electric plants based on the method of failure trees using fuzzy logic in the MATLAB environment. [2,6,8]

# 2. DEVELOPMENT OF SIMULATION SOFTWARE USING FUZZY LOGIC

A frequently used analysis method in a system's reliability study is based on the evaluation of failure probability. In this method the crisp values of failure probabilities for electrical components are generally used in order to compute the systems reliability, based on equivalent reliability diagrams. [5,7]

## 2.1. Definition of input membership functions.

The developed software is using Gaussian membership functions. For this kind of function the mean and standard deviation ( $\sigma$ ) must be specified.

So for every component of the system 7 grades were defined, on a linear interval of failure and repair intensity values ( $\lambda$  and  $\mu$ ) and then the function values are established.

Not acceptable	Ν	0
Almost acceptable	AN	0.167
Close to acceptable	PS	0.333
Acceptable	S	0.5
Good	В	0.667
Almost very good	AFB	0.833
Very good	FB	1

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INPUT MEMBERSHIP FUNCTION

MEDIAN VALUE AND STANDARD DEVIATION COMPUTING

OUTPUT MEMBERSHIP FUNCTION MEDIAN VALUE AND STANDARD

RULE SET MATRIX GENERATION

ŧ

INPUT VALUES SPECIFICATION

DISPLAY OUTPUT CRISP VALUE

Figure 2.

Flowchart of the fuzzy program

GENERATION

DEVIATION COMPUTING

The fuzzy method is presented schematically in figure 1. The fuzzy analysis program generates input membership functions (on basis of specified failure intensity  $\lambda$  and repair intensity  $\mu$ ) and then generates the output membership functions and the rule set. The flowchart of the algorithm is presented in fig. 2.







GUI

All program functions are launched from the "d\_fuzzy.m" module. The GUI window is presented in figure 3.

The "d\_date.m" module is launched on action of "Input data" button. The simulation data input includes  $\lambda$  and  $\mu$  specification, data saving and data reload.

The system equation is input from the "d\_param" and  $\lambda$ and  $\mu$  are input from a separate window which allows as many parameters as many components were specified. The program also allows data saving (the data are saved in a .mat type file) in files with optional names. The saved data can be reloaded in a separate interface from their files which contains all system parameters and also the system equation. Once established the system parameter values for specific runs can be input from the "d\_param\_intr.m" module.

Mean values for membership functions are computed on basis of the relation:

$$F_{i} = \frac{\lambda_{i}}{\lambda_{i} + \mu_{i}}$$
(1)

where i = 1...7, is the number of the membership function according to the earlier defined grade.

Standard deviation ( $\sigma$ ) is computed with asymmetric Gauss function based on relations (2):

$$\sigma_{i,1} = \frac{|F_{i-1} - F_i|}{3}, \qquad \sigma_{i,2} = \frac{|F_i - F_{i+1}|}{3}$$
(2)

After the introduction or reload of data from saved files, we can reenter the main module which gives us two options:

- fuzzy simulation

- decision surfaces display

Choosing "Fuzzy simulation", after computing input membership functions parameters for each system component, the program generates these functions. Decision surface display facilitates the evaluation of the fuzzy outputs.

## 2.2. Definition of output membership function

In order to compute the output membership functions we start with the reduced system schematics from which the failure tree is generated. From the flowchart we can derive the



system's characteristic equation and then the program generates the output membership function.

#### 2.3. Definition of the rule set

The rule set of the fuzzy inference system defines the way in which the inputs and outputs are linked. The rules are described in form of logical relations having as variables linguistic degrees of the inputs and as operators the "and" and "or" logical operators. An example of fuzzy rule is:

### If $elem_1$ is FB and $elem_2$ is B and $elem_3$ is S than the system is B.

After the establishment of the rule set, the program can generate inference surfaces in the input-output space which are in fact the values of the outputs for the whole range of given inputs. Due to the limitations of 3D representation, these surfaces can be represented only as 2 inputs simultaneously, the remaining inputs being considered static for that case. The 2 inputs which are wanted to be represented can be selected in the program interface.

#### 2.4. Simulation results

After generating the membership functions and rule sets the program also generates the so called "fuzzy inference system" information structure. If this structure is used for a single run, then the crisp values of inputs are specified and the "evalfis" function is used for the computation of crisp output values. The program displays this value in a separate window.

## 3. CASE STUDY. TILEAGD ELECTRIC STATION (SE) [2].

In [2] the normal form of SE Tileagd, Bihor County scheme is presented. Evaluation of reliability is realized considering the Săcădat user, positioned on BC - 20kV collector bar and the study criteria is considered in the absence of the consumer.

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File name:	intrari_tileagd_1	Оре	1
Files of type:	MAT-files (*.mat)	▼ Canc	el
Figure	• 4. Data loading	g window foi	• SE

**Figure 4.** Data loading window for SE Tileagd

Using statistical data representing median values of reliability indicators for the equipments in Electric Stations (SE) and also using the equivalent reliability diagram we had reduced the SE Tileagd scheme to an equivalent reliability diagram (DEF) presented in figure 14 a. This diagram was then used to formulate the system equation for the fuzzy simulation. The reduction of normal scheme had been made by transposing it in a scheme in which the elements are connected in series or parallel considering the dimensioning and connection of elements. All feeds for Săcădat consumer, on all path, from the source had been considered. In figures 4-7 input data of analyzed electric station are presented.

In figures 8 -13 the obtained membership function diagrams are presented for SE Tileagd.

Lambda	a minim:	Lambda	a maxim:	Miu min	im:	Miu ma×	im:
1	2.46e-006	1	1.352e-005	1	0.017216	1	0.025262
2	1.42e-006	2	1.122e-005	2	0.017537	2	0.071022
3	7.9e-006	3	1.93e-005	3	0.0045303	3	0.017284
4	1.1e-006	4	4.4e-006	4	0.04	4	0.061401
5	2.8e-006	5	1.4e-005	5	0.85719	5	1.2005
6	2e-007	6	1e-006	6	0.85719	6	1.2005

**Figure 5.**  $\lambda$  and  $\mu$  parameter editing window for SE Tileagd

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Figure 6. Input values loading window for SE Tileagd

#### Figure 7. Simulation data editing window for SE Tileagd



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**Figure 14.** Reduced scheme (a) and scheme of system for SE Tileagd (b)





For computing output membership functions we start from the system scheme from which the failure tree is generated figure 14.

Characteristic equation of the system is deduced from the schemes presented in figure 14 and is given by relation (3):

$$F_{TIL} = 1 - \prod_{i \neq l, 6} (1 - F_i) = 1 - (1 - F_l)(1 - F_2)(1 - F_3)(1 - F_4)(1 - F_5)(1 - F_6)$$
(3)

Relation (3) is used by the program to generate the output membership function presented in figure 15.



Figure 15. Output membership functions generated for SE Tileagd

The program displays the obtained output values in a separate window presented in figure 16. In figures 17 and 18 some decision surfaces are presented.





#### 4. CONCLUSIONS

The use of "fuzzy sets theory" in the study of reliability of electric energy systems and equipments consists in the possibilities offered by quantification and modeling of qualitative enounces – incomplete and altered information, subjective appreciations – in flexible forms, more close to the way of thinking the engineers operates with.

The program developed under MATLAB environment for the fuzzy simulation of reliability of electrical equipments permits the step by step definition of the fuzzy model and it is realized in a versatile manner, object oriented and modular. The program can make diverse simulations, in small times, for a given scheme, in the analyzed fuzzy intervals making possible the visualization of values range in which the non-reliability and reliability of the system can evolve.

The realized evaluations, obtained with the SE reliability fuzzy simulation program, are accurate, in comparison with the values obtained by Monte Carlo method and direct DEF computation [2, 4].

R	FUZZY	MONTE CARLO 10000 simulări	DEF
TILEAGD	0,99808771	0,99822	0,99808

## Comparative results for fuzzy, Monte Carlo and DEF methods

Development of SE fuzzy reliability simulation program using the MATLAB programming environment, based on failure tree method, application of the program for SE Tileagd, Bihor County, and comparative evaluation with the Monte Carlo simulation method results and with DEF analytical method results, are contributions of the authors in this article.

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# VARIABILITY OF GAS-PARTICLE PARTITIONING OF POLYCYCLIC AROMATIC HYDROCARBONS IN A PILOT AREA OF VOJVODINA

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#### **Abstract:**

Polycyclic aromatic hydrocarbons consist of two to eight condensed aromatic rings and they are produced during incomplete combustion of organic materials. High atmospheric levels of polycyclic aromatic hydrocarbons are associated with industrial activities, energy production, and any type of combustion and traffic. In the atmosphere, PAHs are distributed between gaseous and particulate phase. Distribution of PAHs in the atmosphere controls removal processes and atmospheric degradation. During the June and July 2004 air sampling campaign was conducted in the region of Vojvodina, and concentration levels of 16 PAHs in gaseous and particulate phases were determined.

#### Keywords:

Polycyclic aromatic hydrocarbons; Gas-particle partitioning; Atmospheric distribution; Active air sampling

## **1. INTRODUCTION**

Polycyclic aromatic hydrocarbons (PAHs) are the comlex group of organic compounds with planar structure, with C and H atoms organized in circlet structure with at least two aromatic rings. Primary natural sources of PAHs are fires and volcanic eruptions. The most important anthropogenic sources of PAHs in the atmosphere are wood combustion, energy production, and production of aluminium, incineration, catalytic cracking and exhaust gases from vehicles. Concentration levels and behavior of polycyclic aromatic hydrocarbons in the environment have been frequently monitored because of their long-term transport, global distribution and high toxicity [1, 2, 3, 4, 5].

In the atmospheric environment, PAHs are found in the gaseous phase or sorbed at the solid particles, depending mainly on ambient temperature and vapor pressures. Gas-particle partitioning process can be described using partitioning coefficient  $K_p$ :

$$K_{p} = \frac{1}{K_{v}} = \frac{\frac{F}{TSP}}{A}$$
(1)

where:

 $K_P$  –partition coefficient between particle and gaseous phase in atmosphere (m<sup>3</sup> µg<sup>-1</sup>)

 $K_V$  – partition coefficient between gaseous and particle phase in atmosphere (µg m-3)

A i F – compound concentration associated with the gaseous and particle phase, respectively (ng m<sup>-3</sup> air)

*TSP* – total suspended particulate matter concentration ( $\mu$ g aerosol m<sup>-3</sup> air)

Atmospheric distribution of PAHs, can also be described with total amount of supstance proportion sorbed on atmospheric particles,  $\phi$ :

$$\phi = \frac{F}{A+F} = \frac{K_{p} \cdot TSP}{1 + K_{p} \cdot TSP}$$
(2)

During the period from June - July 2004, air sampling campaign was conducted in the region of Vojvodina, Serbia, and concentration levels of 16 US EPA PAHs were determined.



#### 2. MATERIALS AND METHODS

Concentration levels of selected polycyclic aromatic hydrocarbons have been determined in accordance with the sampling procedure and analysis of organic pollutants in ambient air, adopted by EPA [6, 7]. Active air sampling method is realized through flowing of definite quantity of air, controlled by compressor, through the sampler. In the first step, air is released through the horizontally placed single layer filter made of glass fiber (GF), which holds atmospheric particles over 0.1  $\mu$ m in diameter. Air, then, passes through the sorbent made of polyurethane foam (PUF), placed behind GF, which collects gaseous phase of PAHs molecules.

The sampler used for the active sampling of air was GV2360 Thermo Andersen TSP, made of stainless steel boxes and equipped with 20.32 x 25.4 cm filter holder and PUF holder (9 cm in diameter and 30 cm long). Air was passed through using a 1200 watt motor controlled by an inverter (Hitachi L100-015NPE) and flow was measured by a Sierra 620 fast flow insertion mass flow meter with a totaliser. The average total sampled air was 1200 m<sup>3</sup>/day. For each sampling period, per one Whatman grade G653 glass fiber filter (dimension:  $20.32 \times 25.4$  cm) and two polyurethane foam filters (dimension: 9 cm diameter and 5 cm long) were used.

Prior the sampling, glass fiber filters were burned in 400°C for 5 hours and polyurethane foam filters were Soxhlet extracted by 1:1 acetone/hexane (Merk suprasolv) by a Foss Tecator Soxtec 1045 HT-2 apparatus for 4 hours to 120°C.

After the sampling period (3 x 24h), GFs and PUFs were extracted and analzyed using GC/MS method. Analytical determination of 16 EPA PAHs in all samples was carried out in laboratories of Research Centre for Environmental Chemistry and Ecotoxicology (RECETOX), Masaryk University in Brno, Czech Republic.

## **3. RESULTS**

Three 24-hour high volume samples were collected from each of three sampling sites in in the town of Pančevo, Vojvodina, Serbia. Air sampling campaign in Pančevo was conducted during the period from 27th – 30th June, 2004. Two samplers were placed within the industrial area, in the yard of the oil refinery and petrochemical complex (localities P1 and P2, respectively). The third HiVol sampler was placed in the city center, on the top of the Pančevo city hall (locality P3). Detailed information on the three sampling spots is presented in Table 1. Concentration levels of 16 EPA PAHs are presented in Table 2.

Site ID	Latitude	Longitude	Elevation (m a.s.l.)
P1	N 44°49' 56.3"	E 20°41' 25.4"	82
P2	N 44°49' 57.0"	E 20°40' 17.0"	85
P3	N 44°52' 12.8"	E 20°38' 24.1"	130

Table 1. Detailed information on the sampling sites

Sample type	PUF	GF	PUF	GF	PUF	GF
Locality	P1 P2			P3		
Sampling period	27-30th June 2004					
Nap	1.195	0.010	0.811	0.016	0.454	0.010
Acy	0.065	0.003	0.050	0.001	0.044	0.001
Ace	0.063	0.006	0.054	0.006	0.027	0.002
Flo	1.454	0.003	1.497	0.009	0.171	0.002
Phe	18.309	0.041	27.364	0.144	3.659	0.030
Ant	0.679	0.001	1.152	0.007	0.187	0.002
Flu	2.133	0.024	10.997	0.167	2.160	0.071
Pyr	1.521	0.020	3.773	0.095	1.831	0.077
B(a)A	0.023	0.008	0.017	0.018	0.070	0.028
Chr	0.120	0.018	0.146	0.066	0.206	0.088
B(b)F	0.041	0.045	0.019	0.220	0.029	0.380
B(k)F	0.022	0.030	0.010	0.122	0.012	0.144
B(a)P	0.021	0.016	0.006	0.102	0.000	0.130
I(1,2,3-cd)P	0.021	0.046	0.005	0.240	0.000	0.365
D(ah)A	0.000	0.002	0.000	0.013	0.000	0.024
B(ghi)P	0.035	0.066	0.009	0.320	0.000	0.500
Total	5.700	0.336	45.909	1.547	8.849	1.853

Table 2. Average concentrations of PAHs in gaseous and particulate phase  $(ng/m^3)$ 

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Estimated distribution of polycyclic aromatic hydrocarbons between gaseous and particulate phase in the ambient air of Pancevo is shown in Figures 1 - 3.



Figure 3. PAH distribution between gaseous and particulate phase at locality P3

In the city of Novi Sad, the highest total concetraton level of examined PAHs was detected on the locality P2 (Petrochemical complex Pancevo) and equals  $\Sigma$ PAH=47.456 ng/m<sup>3</sup>. Total concentration of PAHs at the localities P1 (oil refinery) and P3 (city center) are  $\Sigma$ PAH=26.036 ng/m<sup>3</sup> and  $\Sigma$ PAH=10.747 ng/m<sup>3</sup>, respectively.

In national legislation, maximum allowed concentration of examined group of persistent organic pollutants has not been defined, therefore comparison with legallly adopted values was not possible. Threshold value of ambient air quality for benzo(a)pyrene for 24-hour sample, 0.1 ng/m<sup>3</sup>, has been



exceeded at the localities P2 and P3, with value 0.108  $ng/m^3$  for locality P2 and 0.130  $ng/m^3$  for locality P3.

Obtained experimental results point out on almost complete particle sorption of pollutants B(b)F, B(k)F, B(a)P, I(1,2,3-cd)P, D(ah)A i B(ghi)P, with exception of sampling site P1 (Oil Refinery Pancevo), where foregoing PAHs fractions, beside D(ah)A, are about 50%. Specific distribution of polycyclic aromatic hydrocarbons at oil refinery, does not manifest, apriory, low concentration of total suspended particles in the atmosphere. Increased concentration levels of PAHs in gasous phase or sorbed at ultrafine particles which can not be collected at glass fibre filters, issued from refinery, are probably responsible for atmospheric distribution of PAHs at site P1.

## 4. CONCLUSIONS

Results of analysis point out on the presence of residual quantities of PAHs in air samples from three localities in the town of Pančevo.

The highest concentrations of examined polycyclic aromatic hydrocarbons was detected at the petrochemical complex  $(47.456 \text{ ng/m}^3)$ .

Regulation defines limit value of ambient air quality only for benzo(a)pyrene (0,1 ng/m<sup>3</sup> for 24hour sample). Limit value was exceeded at two selected localities in Pančevo – petrochemical complex (0.108 ng/m<sup>3</sup>) and city center (0.130 ng/m<sup>3</sup>).

Direct influence of atmospheric distribution on wet and dry deposition processes, long-range transport, as well as potential reactions of degradation of PAHs in the atmosphere, points out on an extreme importance of examination and determination of concentration levels and partition of pollutants in the atmosphere.

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# ADVANTAGE OF THE SUBSTITUTION ETHYLMERCAPTAN, COMPOUND FOR ODORIZATION NATURAL GAS, WITH TETRAHYDROTHIOPHEN

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#### **Abstract:**

This paper presents the advantage of substitution ethylmercaptan, compound for odorization natural gas, with other compound for odorization, tetrahydrothiophen. The physical - chemical properties of both compounds, ecological - toxic characteristics, odorization properties and evaluation of annual consumption odorization compounds in Serbia are discussed. The comparative analysis of these two odorization compounds from the aspect of chemical stability in the system of gas installations and economic acceptability have been described.

## Keywords:

Ethylmercaptan, tetrahydrothiophen, odorization, substitution

# **1. INTRODUCTION**

Natural gas, in particular, which is distributed for consumer goods, must be odorized up to level of one fifth of the lower flammable limit for security and health safety reasons.

Odorization compound with their physical - chemical properties should ensure first of all recognizable strong smell from a small portion of evaporation, or in a low concentration level to be detected leakage of gas and prevent unwanted consequences.

In Serbia as odorant, almost exclusively, used ethylmercaptan characterized with the best ability odorization, are no longer used in most European countries.

One of the main reasons for the termination of the use of ethylmercaptan as odorant its chemical instability (in the reaction with air and iron-oxide), which causes loss of smell intensity, as well as changes characteristic strong unpleasant smell.

Most frequently used compound for odorization natural gas is tetrahydrothiophen which has recognized intensive smell. It is the most stable of all gas odorants. Tetrahydrothiophen not react with iron oxides and bases and it does not change, nor the intensity or character of smell, for the most causes of loss of smell.

Unlike ethylmercaptan, which is extremely toxic to flora and fauna biosystem and the environment, tetrahydrothiophen belongs to the middle toxic group pollutant and there is no label danger for the environment according to the German classification for surface water pollutants. [4]

# 2. ETHYLMERCAPTAN (EM)

## **Physical - chemical characteristics:**

- ♣ Chemical formula: C<sub>2</sub>H<sub>6</sub>S
- 4 Appearance and the smell: colourless liquid reminiscent of the smell of garlic
- 4 Melting point: -148 °C
- **Boiling point: 35 °C**
- 4 Density (g cm<sup>-3</sup>): 0.839
- ✤ Flash point: -45 °C
- Explosion limits: 2.8 18.2 %
- ✤ Water solubility: slight



#### Other properties of ethylmercaptan:

- 4 In normal circumstances, a stable, but extremely flammable liquid;
- Incompatible materials: oxidans (can lead to flammable), strong acid (reaction can be violent), calcium chloride (react violently), corrosive effect on metals, reacts violently with alkaline metals;
- Classification, belongs to the 3rd group of toxins and is extremely toxic to flora and fauna and surface water;
- UN number 2363;
- Additional tag 336; [5]

## Ethylmercaptan as natural gas odorant

Ethylmercaptan has a very strong and unpleasant smell reminiscent of the smell of garlic. Threshold of low sensitivity of smell defined EM, based on its odorization capacity, as the best odorization compound for the natural gas. However, the big problem is nonstability of ethylmercaptan because it easily reacts with oxides and bases giving disulfide, and in that case loosing smell properties.

In addition, irreversible adsorption of ethylmercaptan on the walls of steel and polyethylene gas pipes increases ethylmercaptan consumption.

Low flammablity and extreme toxicity, associate with environmental and contamination aspect are the problems, because increase the cost of transport and storage. For these reasons ethylmercaptan as odorant need to replace with other substances with a higher chemical stability and less or slightly toxicity for the environment. [4]

## Assessment of consumption ethylmercaptan in Serbia

According to company for natural gas odorization "OD – JU" from Ruma, the total amount of odorized gas in 2007. year was about 517,500,000 Sm<sup>3</sup>. Total consumption of ethylmercaptan was about 6700kg, with the average achieved concentration about 12.95 mg/Sm<sup>3</sup> of natural gas. [3]

## **3. TETRAHYDROTHIOPHEN (THT)**

#### **Physical - chemical characteristics:**

- 4 Chemical formula:  $C_4H_8S$
- 4 Physical state and appearance: Liquid.
- 4 Odor: strong unpleasant
- Molecular Weight: 120.11 g/mole
- 4 Color: Clear Colorless.
- Boiling Point: 284.5°C
- Melting Point: 27.4°C
- ↓ Density: 1.26 (Water = 1)

## Information about toxicity:

- 🖕 Acute oral LD50 (in rats)
- Acute inhalation LC50 (in mice)

2450mg/kg 27g/Sm<sup>3</sup> (2 hours)

Environmental information:

Information about toxicity for aquatic organisms: No data available Toxicity to Animals:

Acute oral toxicity (LD50): 1900 mg/kg [Mouse].

Acute dermal toxicity (LD50): >3800 mg/kg [Rat].

## Tetrahydrothiophen as natural gas odorant

Tetrahydrothiophen has recognizable characteristic strong smell that is different from other spices impurities that may appear in the natural gas. THT shows very small deviations from own specific fragrance and is very difficult to overdose.

Tetrahydrothiophen is the most stable of all gas odorants, as a result of heterocyclic chemical structure, what is unusual for other common odorants. Tetrahydrothiophen not react with iron oxides and bases, and is imperceptible to most of the causes of pad smell.

Adsorption of tetrahydrothiophen on the walls of the new pipe is almost completely reversible so that the amount of THT is a reserve of odorant. In the case of changes in the dosage THT, dynamic equilibrium adsorption and desorption are disturbing and THT is desorbed from the wall of pipes back into the gas.

THT is in the middle group of pollutants according to the German classification of pollutants surface water (W6K2) and not wearing the label of danger for the environment, which makes it easier for packaging, storage and transport. [1, 4]



## 4. COMPARATIVE ANALYSIS OF ETHYLMERCAPTAN AND TETRAHYDROTHIOPHEN AS ODORANTS

## **Stability**

The difference in stability ethylmercaptan and tetrahydrothiophen in the presence of corrosion on the walls of pipes is a significant benefit for the THT, which could be displayed in the chart (Figure 1).





From the diagram it could be seen that the concentration of THT in the gas begins to decline significantly after the third day, while the concentration of EM decline in the "o" for about 2 hours. This means that the EM is totaly spent in the chemical reaction of oxidation, loosing completely smell in a very short time. [4]

## **Economic effects**

Comparative analysis of the costs of the odorization with EM and THT in the following text is calculated for concentrations of odorant in the natural gas of 12.95 mg/Sm3 for odorization 517.500.000Sm<sup>3</sup>/vr, the average distance from odorants storage is about 80km.

# **Odorant ethylmercaptan**

Total amount of required odorant is 517.500.000 Sm3/yr • 0.00001295 kg/Sm3 = 6700 kg/yr. Price of charging for EM is 16.10 €/kg, (or 0.000241 €/Sm<sup>3</sup>).

The annual price for EM is 16.10  $\epsilon/kg \cdot 6700 \text{ kg/god} = 107.850 \epsilon/vr$ .

## **Odorant tetrahydrothiophen**

Total amount of required odorant is 517.500.000  $\text{Sm}^3/\text{vr} \cdot 0.00001295 \text{ kg/Sm}^3 = 6700 \text{ kg/vr}$ . Price of charging for THT is 31.02 C/kg, (or  $0.000465 \text{ C/Sm}^3$ ). The annual price for THT is  $31.02 \text{ C/kg} \cdot 6700 \text{ kg/god} = 207,850 \text{ C/yr}$ . [3]

# **5. CONCLUSION**

Replacement and substitution of ethylmercaptan by THT as the odorant for natural gas, is obviously required for the following reasons:

- For the protection of the environment bearing in mind its outstanding cumulative and biocumulativ toxic effect for flora, fauna, biosystem and environmental in general:
- Ethylmercaptan has unstable smell properties especially in the presence of oxide and base. This is particularly expressed in equipment and installations with compressed natural gas (LPG) for the cars:
- In Europe are generaly not used ethylmercaptan for odorization natural gas. 4
- The harmonization between national and international (EU) laws of regulations in the field of natural gas odorization with the EU.

According to real estimation, of the replacement procedure ethylmercaptan by tetrahydrothiophen can be completed in the next 3 to 4 years. [3, 4]



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# QUANTITY AND RECYCLABILITY OF Fe - METALS AT THE END-OF-LIFE VEHICLES IN REPUBLIC OF SERBIA

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#### **Abstract:**

The growth of the world's population has determined the need for faster, simpler and easier communication. Due to such communication, along with modern social - economic and industrial development, the number of vehicles has largely increased. At the end of life, vehicles represent a potential threat to the environment. This paper gives a statistical view of the number of registered vehicles by brands in Serbia. The amount of Fe – metals by vehicle dismantling, and the possibility of their recycling is shown. It was pointed out the necessity of harmonization of our laws which regulates this area with the laws of the EU, as well as the need for implementation of appropriate ISO standard in the Republic of Serbia.

## Key Words:

Statistic data, ISO standard, Fe-metals, recyclability

# **1. INTRODUCTION**

In order to minimize the impact of vehicles disposal on the environment, the End-of-Life Vehicles Directive (2000/53/EC) aims to promote the collection, reuse and recycling of their components. Generally speaking, there are few problems if the vehicles are disposed and not recycled, like occupying the landfill space, potential leakages of fuel and motor oil into water recipient and soil, emissions of volatile compounds, and possible fires. Some of the components are classified as harmful or either hazardous to the environment. Those problems are still present in recycling operation, if the dismantling operations are not handled by regulations, and this means that all fluids (oil, fuel, windshield washer fluid, antifreeze, brake liquids, etc), batteries, and other nonmetal parts should be extracted.

In Serbia, the recycling business is present but the most of them are recycling just one sort of material or car parts. For now, the new products are being exported and some of these parts, like batteries, are reused. Fuels are being sent to oil refinery, tires are used in cement industry in combustion processes, but shredder dust, textiles, car seats, glass and some other parts are being landfilled. [2]

# 2. THE STATISTICS OF REGISTERED CARS IN SERBIA

According to data from project "Razvoj integrisanog i održivog sistema reciklaže motornih vozila na kraju životnog ciklusa u Srbiji", in Serbia are 1.534.658 registered passanger vehicles in 2008. [3]

In Serbia, almost one third of total population owns "Zastava" (31%), followed by "Opel" (18%), "Volkswagen" (16%), "Lada", "Fiat" and "Reno" (7%). [3]



# **3. AMOUNTS OF FE-METALS AND RECYCLING POTENTIONAL BY VEHICLE DISMANTLING**

The car is a product of high complexity for whose benefit in the production is used more than hundred different technologies and that are built around 15 000 parts. Car parts are produced from different materials. The total weight of the current passenger car is represented by iron and steel.

The European Union Directive said that the acquisition of vehicles at the end of the life cycle of vehicles and parts should be organized by the state. It is necessary to provide storage and the space to be made by the treatment of spent vehicles and their components.

International Standard ISO 22628 in 2002 very clearly define the issue of recycling of passenger vehicles, which is not the case in Serbia where there is no standard for this. ISO 22628 also defines and recyclability rate (percentage by mass of the new vehicle potentially able to be recycled, reused or both), and recoverability rate (percentage by mass of the new vehicle potentially able to be recovered, reused or both), as shown in the figure 2. [2, 4]

	Reco	Undefined residue		
(Component parts)	(Materials)	(Materials)	(Materials)	
Re-use	Recycling	Energy recovery		
Recyclab	ility rate <sup>a</sup>			
Recoverability rate <sup>a</sup>				
Vehicle mass				

Figure 2. Material distribution of the total mass of vehicles for the further treatment [4]

Almost a third of passenger cars in Serbia are the brand "Zastava" (which is about 511.553 vehicles), which presents models "Koral", "Skala" and "Florida" by one-third (approximately 170.517 vehicles). [1, 3]

Potential for recycling Fe-metals from vehicles "Zastava" is calculated by the following formula:

Number of vehicles from particular model "Zastava" × vehicle weight × percentage of Fe-metals in vehicle × rate of recyclability

Model of	Numbor	Vehicle	Percentage of	Rate of	Fe-Metals recyclability
Zastava car	of vobialog	weight	Fe-metals	recyclability	potential
(Fiat Auto)	of vehicles	[kg]	[%]	[%]	[kg]
Koral	170.517	807	73.6	62.0	62.792.926
Skala	170.517	835	75.0	62.0	66.207.488
Florida	170.517	950	73.6	62.0	73.919.801
				Total	202.920.215

Table 1. Recyclability potential of Fe-metals in "Zastava" vehicles [1]







in the Zastava Florida [1]



# 4. CONCLUSION

In this analysis is shown the potential for recycling Fe-metals only from vehicles brand "Zastava", which makes one third of the total number of registered passenger cars in Serbia (according to data for 2008. yr.). The remaining two thirds are foreign vehicle manufacturers with much greater potential for recycling, because they are more massive and have higher rate of recyclability. Serbia has significant capacity for processing Fe-metals, so vehicles for recycling are an important resource.

For accession Serbia to EU, it is necessary to enact a law that regulates this area, and harmonize it with EU legislation. [1, 3]

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# SLAG – UTILISATION IN ROAD CONSTRUCTION – EXPERIENCE AND SOLUTIONS

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# **1. INTRODUCTION**

As the world population grows, so do the amount and type of waste being generated. Many of the wastes produced today will remain in the environment for hundreds, perhaps thousands, of years. The creation of nondecaying waste materials, combined with a growing consumer population, has resulted in a waste disposal crisis. One solution to this crisis lies in recycling waste into useful products. One answer to all of these problems lies in the ability of society to develop beneficial uses for these waste products.

The road-highway construction industry can effectively use large quantities of diverse materials. The use of waste by-products in lieu of virgin materials for instance, would relieve some of the burden associated with disposal and may provide an inexpensive and advantageous construction product. Current research on the beneficial use of waste byproducts as road-highway construction materials has identified several promising uses for these materials. Some of these materials include: Blast furnace and steel slags.

# 2. STEEL SLAG IN EUROPE

In Europe are produced annually around 15 Mil tones of steel slag, resulting from different type of steel technology (Figure 1),

More than 75 % of steel slag was recycled in Europe (Figure 2.) in different kind of utilization in especial like raw materials.



Figure 1. Type of steel slag





Figure 2. Slag utilization in Europe

## 2.1. European waste framework Directive

Present situation in the steel industry on material management give as an overview on the legal situation regarding the dealings with by-products such as slag and secondary raw materials on the basis of the European waste framework directive. Further on it describe the existing frameworks nebulous differentiation between waste and non waste (by products, when ceases waste to be waste) that lead to a flood of court procedures and to a discrimination of by-products and products made of recycled materials. Metallurgical slag is given as an example for a purposeful produced by-product in the steel industry which replaced primary raw materials and thus saving resources. Typical product criteria are described. Finally the proposal on the revision of the waste framework directive of the European Commission and those presently discussed in Parliament and Council is evaluated regarding the necessary clarification

- when a substance is excluded from the waste legislation as (by-)product, or

- when it creases to be secondary row material

A discrimination of by-products and products made of recycling material compared to products made of virgin material is not acceptable and contrary to the aim of sustainable management. On the contrary the usage of by-products and secondary row-materials must have priority.

European Waste Catalogue does only name unprocessed slag as a waste, European Waste Shipment Regulation (NO 259/93) - GREEN LIST, GC 070 exclude processed slag from the waste list:

"Slags arising from the manufacture of iron and steel (including low alloy steel) excluding those slags which have been specifically produced to meet both national and relevant international requirements and standards."

Green list substances shall be generally excluded from control procedures of the regulation since such waste should normally not present a risk to environment.

Principles of European Waste management say that steel slag has to be recycled (Figure 3.).





Figure 3. Waste management hierarchy

# 3. DESCRIPTION OF THE EXPERIMENTAL SETUP

3.1. Steel slag treatment process

Steel slag type	Treatment	
Hot slag from EAF	Cooling by water	Quick cooling is important for technical
	spraying	and environmental properties (Figure 4)
Raw slag with steel	Iron separation	Steel recovery pays for the slag
_		treatment (Figure 5)
Raw slag	Crushing and	Crushing and screening gives different
_	screening	products (Figure 5)
Slag products	Road aggregates rip	Products differ only in grain size
	rap chippings	distribution (Figure 6.)

# Table 1. Main slag processing

Main slag processing is mechanical treatment of cold slag, the principle of slag processing are in Table 1.



Figure 4. Cooling area with water spraying





Figure 5. Instalation of slag treatment SPS Hunedoara



Figure 6. Slag products

## 3.2. Steel slag in Road construction

CLOOS Luxemburg had more than 100 years experience in utilization of slag in road construction, an examples of road layers (Figure 6.)

Slag crushing aggregates can be used in all layers of the road, in Romania; SPS homologated the shape, foundation, basic and binder layers and are in course of homologation the utilization of slag in asphalt layer. Here will be used cold slag treatment procedure for obtain good results.

Terminologie des couches et performances des matériaux utilisés









In Figure 7. we can see red line, property of slag product 0-45; and minimum and maximum requirement of EN 13242,

Example of slag utilization in road construction in Hinedoara is the 4 bands road between Deva and Hunedoara (Figure 8), where the basic, foundation and binder was made from slag aggregates from Buituri Slag Dump, processing by SPS. Unfortunately the Romanian road designers and constructors don't understand yet to use this waste; by-products existing in Hunedoara in Slag Dump in quantity of 70 Mill. Tones.

SPS continue the researches regarding slag utilization in road construction with University "Politehnica" Timisoara – Road Construction Department, now in researches of Slag roads comportment in different charges starting with County roads, Villages roads, technological roads, and sure Highway.



Figure 8. Slag road construction; Hunedoara - Deva

# 4. ANALYSIS OF RESULTS AND CONCLUSIONS

## 4.1. Product Certification and Quality Control

Steel slag has to undergo a quality control process like any other process (Table 2.), steel slag is an artificial stone, with the request property for road construction, and other utilizations: concrete production, fertilization, hydraulic construction, building foundation, etc.



No.	INDICATORS	VALUE
	Bulk density according to	Average value: 2,06 g/cm3 for grain size
1	DIN 52110	mixture 0/32 and 0/45
T	Proctor density according to DIN	Average value: 2,47 g/cm3 for grain size
2	18127	mixture 0/32 and 0/45
T	Fines	In grain size range $0,0 - 0,063$ mm from $0,2$ to
3		0,4 weight%.
4	Destruction by beating SZ 8/12	Desired value 18,0 weight-% for chippings
5	Destruction by beating SD 10	Desired value 26,0 weight-%
6	Polished stone value (PSV)	PSV 60, chippings for asphalt
7	Frost resistance	Limit value 3,0 weight%
8	Volume stability	Limit value 5,0 vol%
9	Inner angle of incline	Average value 40 °

Table 2. List of technical test

Slag Processing Service SA Hunedoara (CLOOS Luxemburg is main shareholders with 80% of shares), start the work in ArcelorMittal Hunedoara Slag Dump, with chemical and physical tests of the slag, make in Luxemburg (80 tones of samples taken from different places from slag dump was send with tracks). After this was start the treatments of old slag: crushing and screening, iron separation, aggregates rip rap chippings, with 500.000 tones/year capacity Installation.



Figure 9. Conformity Certificate

Conformity Certificate for slag aggregates utilization in Romania (Figure 5.), was obtain by SPS in 2006, was certificate that the products "Crashing Aggregates from Steel Slag" 0-4; 4-8; 8-16; 16-31,5; 31,5-63; si 0-63, produces by SPS in Slag Dump Buituri Hunedoara, are in accordance with: EN 12620/2002, EN 13242: 2002/AC:2004, Utilization domain: construction of: roads, civil and industrial buildings, hydraulic and earth construction.

4.2. Comparatives cost of slag roads and virgin materials roads

We analyze comparatives structure of road layers; classic and two alternatives for basic and foundation layers, (Figure10.) mentioned that wear layer in all three situations remain the same asphalt mixture and the existing shape also.



Thickness	Layer – CLASSIC
5 mm	Wear - asphalt mixture
	Basic - natural
20 mm	crash stone
	Foundation -Ballast 0-63
30 mm	mm
X mm	Shape - existing

Thickness	Layer- Alternative 1	Layer- Alternative 2
4 mm	Wear - asphalt mixture	Wear - asphalt mixture
15 mm	Basic - slag 0-63 mm	Slag - optimal mixture
20 mm	Foundation -Slag 0-150	stabilizated with: 0.5 ciment and 8% water
X mm	Shape - existing	Shape - existing

Figure 10. Comparative layers classic-slag roads

The comparative costs in "LEI" of all three variants (Figure 11.):

- 1. Classic system road (virgin materials)
- 2. Alternative 1 road system with slag
- 3. Alternative 2 road system with slag and cement

Sow as that the partial slag roads analyze are with 24% chipper that classic roads. If the road will be executed integrally by slag products like in Luxemburg, Germany, France, etc. the cost reduction is around 40%.



Figure 11. Comparatives cost of the roads

Conclusions: We can construct with the same amount 140% more roads. This is not the single reason for using slag, the durability, stability of the roads is better and not the last we save virgin materials, recycling the slag and ensuring the slag dump disappear.

Use of steel slag is absolutely necessary in Europe to reduce costs and to comply with environmental laws

- Slag use in Europe has a long tradition.
- European law asks for recycling of steel slag.
- European legislation makes it sometimes difficult to bring slag products to the market.
- Process technology is known and proven.
- Slag products can be certified and have to undergo a quality control procedure.



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# ENERGY STORAGE IN SOLAR COLLECTOR SYSTEMS WITH PCM SOLAR TANK

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# ABSTRACT

The one of the most important parts of a solar collector system is the solar tank. The correct type and capacity of the solar tank is a requirement of the good operation of the system.

It is necessary to apply a solar tank because the period of the sunshine does not coincide with the time of the hot water consumption generally.

According the current architectural tendecies the boiler rooms are smaller, so the putting of the currently available solar tanks are very difficult. It is necessary to solve the energy storage in a little space. The solution of the problem is the solar tank particularly filled with phase change material. This tank has smaller dimensions and bigger heat capacity than the conventional tanks.

We have made several conception plans to analyze and compare the advantages and disadvantages.