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INNOVATIVE METHODS AND TECHNOLOGY FOR DERIVATION OF CARBOHYDRATE-SILICONE CONTAINING MATERIALS FROM WASTE BIOMASS

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Abstract: *Exhaustion of global reserves of mineral raw materials and fossil energy sources, periodically arising energy crises, and environmental pollution are among the major challenges facing modern society. In the search for new alternative energy and raw materials sources, increasing attention is paid to the processing of industrial, household and agricultural waste into valuable products for the practice. It is of paramount importance in this case to create technologies that are economically viable in achieving the ultimate goal. From renewable agricultural waste, waste from rice production deserves particular attention. The processing of the barley, which separates the grain from the skin, is associated with the accumulation of rice husks, representing about 20 wt. % of total raw material.*

From this point of view, the high content of amorphous SiO_2 *and pure carbon in rice husks defines them as a promising cheap, ecological and renewable raw source of Si and C.*

Keywords: *Efficiency, Effectiveness, Environmental protection, Methods, Model.*

INTRODUCTION

Exhaustion of global reserves of mineral raw materials and fossil energy sources, periodically arising energy crises, and environmental pollution are among the major challenges facing modern society. In the search for new alternative energy and raw materials sources, increasing attention is paid to the processing of industrial, household and agricultural waste into valuable products for the practice. It is of paramount importance in this case to create technologies that are economically viable in achieving the ultimate goal.

From renewable agricultural waste, waste from rice production deserves particular attention. The processing of the barley, which separates the grain from the skin, is associated with the accumulation of rice husks, representing about 20 wt. % of total raw material.

Given the fact, that rice is one of the most widespread agricultures worldwide, and one which may give 3-4 harvests per year depending on the geolocation, the potential amounts of the waste biomass are assessed at approximately 130 million tons. The high content of cinders, the low caloric value and low nutrition values of the said biomass present serious ecological problems. At the present moment there still isn't an effective solution on its utilization, which adds further to the negatives.

In view of those introductory notes, the goal of the present paper is to analyse the possibilities of ecologic and resource effective incorporation of secondary (waste) products, which are being generated during rice production within the state, with the use of innovative methods and technologies.

In order to attain the goal, as set forth, it is necessary to perform the following tasks:

1. Perform a detailed analyses of the current state of rice production within the country – sown and reaped areas, territorial distribution, quantity characteristic and average harvests, perspectives on the industry development, etc.;
2. Review of the possibilities to utilise the secondary (waste) rice production mass with the aid of thermochemical methods in order to extract and use the carbohydrate-silicon containing components present;
3. Offer a principal technological scheme of extraction and utilisation of the carbohydrate-silicon containing and detailed description of the technological positions.

EXPOSITION

Rice production in our country has more than 500 years' worth of tradition, it has taken its stand against dynamic times and it has established itself as a sub industry with a significant economic, social and ecological necessity.

Growing rice within the current territory of the Bulgarian state dates all the way back to the first Ottoman invasions in the Balkan peninsula during the second half of XIV century. Initially, the planting of this grain spanned the rivers Maritsa and Tundzha and their influxes, and later on it took place in the lands along the river Danube.

Due to its specifics, the rice growing serves as a balancing unit in the use of watering resources, as the majority of the latter (circa 70%) are made during the night, i.e. they would leave the country as the river flows. The development of this industry also helps and favours the development of hydromeliorative systems and has influence over the development of watering agriculture within the state in general.

Rice watering fields form ecosystems of their own, thus supporting the biological diversity and the equilibrium between the various flora and fauna, living both in the said fields and in the areas around them. These fields have a decisive effect over the propagation of underground watering horizons. Apart from all that, they create conditions to maintain high soil and atmosphere humidity in the surrounding zones, which boosts productivity of other agricultures.

As far as the land used goes, the country has approximately 25 000 ha of rice watering fields, disposing of a modern watering and drainage systems, as well as with all the necessary equipment, as the larger part of the ducts are covered with concrete.

The construction of the first ever rice watering fields of this type was launched in 1962 when two areas of 250 and 300 acres, located in the village of Voysil and the town of Saedinenie, became the first testing sections. Later on, in 1965, the mass construction of those facilities was launched.

Construction peaked between the 70s and the 80s when our country reached the maximum of 24 700 ha, out of which 18 500 were dedicated to rice crops. The reminder of the areas was used for crops rotation, and in the cases of water shortages in the years to come it was just planted with rice again.

At the present moment almost 16 000 ha of these fields are still good to exploit and allow for the implementation of innovative methods and integration of contemporary technology and scientific results in rice production.

In the transition years, analogously to other agricultural industries, rice planting also allowed a catastrophic drop of areas by a factor greater than 10, which led to 1995 when rice planted fields were merely 1 380 ha. Luckily, during the years to come the industry had its renaissance.

The latitude of the zones, which host most of the rice watering fields (mostly in the regions of Plovdiv, Pazardzhik and Stara Zagora) corresponds to some of the greatest rice produces in Europe – Italy and France. Also, some of the other parameters match quite nicely – such as average monthly rains, average monthly air temperatures, number of days with continuous sunshine and so on.

The predominant type of soil, on which rice production takes place is alluvial soil, which makes them extremely appropriate for rice crops and allows good harvest with relatively modest use of water – about 20 000 - 24 000 m^3/ha.

This complex of soil-climate and infrastructural particularities within the country is ideal to grow early, mid-early and mid-late rice crops, which are characterised by high productivity and excellent nutrition and taste qualities.

According to the statistics of the Ministry of Agriculture, Food and Forestry in 2017 (table 1) 10 486 ha were planted with rice, out of which 10 434 were successfully harvested. As a result, Bulgaria obtained over 58 000 t grain, as based on that harvest, the amount of rice husks, generated in Bulgaria exceeds 10 000 t.

Table 1. Excerpt from Bulletin № 343 – June 2018 by the MAFF,
Areas, average harvests and manufacture from agricultures – harvest 2017

Crops	Sown areas (ha)	Harvested areas (ha)	Average harvests (kg/ha)	Manufacture (t)	Humidity (%)	Impurities (%)
Wheat, wild wheat and spelt	1 147 208	1 144 519	5 358	6 132 671	11.4	2.2
including regular wheat, wild wheat and spelt	*1 136 37*	*1 133 695*	*5 370*	*6 087 537*	*11.4*	*2.2*
Rye	8 424	8 237	2 101	17 304	8.1	4.7
Barley	128 990	128 365	4 637	595 237	10.9	2.5
Oats	13 539	13 266	2 401	31 849	8.9	4.2
Grain corn	400 886	398 152	6 436	2 562 569	12.4	2.5
Triticale	18 677	18 660	3 169	59 140	11.9	3.8
Sorgo	4 424	4 238	2 883	12 219	12.2	2.8
Millet	2 483	2 460	1 802	4 432	12.4	2.7
Buckwheat and other cereals	988	936	2 032	1 902	-	-
Rice	10 486	10 434	5 609	58 523	11.4	2.1

The use of rice husks as a raw material to produce materials, which are applicable in different industries and which are carbohydrate-silicon based, is the subject of a great deal of scientific papers and patents. The available information in the scientific and patent literature forms a few areas of research and use of this particular waste.

One utilisation strategy is with the aid of thermochemical methods. The cinders, obtained from the rice husks burning in a controlled environment contains more than 98% amorphous silicon dioxide and some accompanying substances. The percentage ratio and the concentrations of these components depend on a number of precise conditions. Therefore, this waste could be viewed as a natural, alternative and cheap source of amorphous silicon dioxide – a unique raw material to obtain different silicon-containing materials with industrial and technological applicability.

One specific characteristic of rice is that its metabolism is related to soil extraction and accumulation, in all parts of the plant, and mainly in the external epidermal layer, of the rice husk, of hydrated amorphous silicon dioxide.

Here is why the cinders residue, obtained after the burning of rice husks in an oxidising environment contains primarily silicon dioxide. The cinders residue in rice husks varies between 18 and 23 %, depending on agro technical procedures, soil and climate conditions, under which the plant is grown. It is well known fact, that the organic part of rice husks is comprised of cellulose, lignin and hemicellulose is different ratio, which corresponds to 38 w/% of the total carbon content.

From this perspective, the high content of amorphous SiO_2 and pure carbon in rice husks sets them off as a promising, cheap, eco-friendly and renewable raw source of Si and C. The grainy structure of the husks, their phase composure, their chemical stability, the water insolvability and their high mechanical strength makes them ideal candidates to obtain new functional materials with added value. One must also consider that this waste also has, although not as high (15-20 $MJ.kg^{-1}$), caloric effect.

The properties of the cinders are strongly dependent in the oxidation of the raw material. The low-carbon or carbon-free cinders could be used in many applications, which require pure amorphous SiO_2. Such applications are all manufacturing processes, which use such forms of silicon dioxide, for example: diatomite, “white cinders” or “aerosil”.

Rice husks cinders could also be used in pharmacy, perfumery porcelain, glass, textile, plastic and paper industries, for the production of quartz goods, luminophores, abrasives, casting forms, isolation materials, as well as a raw material for water solvable silicates. Silicon dioxide, produced from rice husks, does not contain impurities, such as boron and arsenic, which makes it a perspective raw material to obtain pure polycrystalline silicon.

Amorphous silicon dioxide with high purity, small particle size and high specific density, obtained from rice husks is considered a great carrier for different catalysts. There is a method to produce cordierite powders from rice husks cinders. Between the various options to utilise the rice husks cinders, a particular field of interest is its use as a raw material to derive zeolites.

Denying the fact, that the cinders residue after burning the rice husks is actually amorphous silicon dioxide, a lot of scientific research head towards its use as puzzolanic materials.

There is data on the possibilities to use “white cinders” as adsorbent to purify water solutions from ions of various heavy metals, as well as to purify industrial waste waters from various organic pollutants.

Other than amorphous silicon dioxide, rice husks contain about 38% pure carbon. That is why, after the appropriate thermal treatment, they could also be viewed as a potential, cheap and renewable raw material to obtain:

- silicon carbide – a material used to produce robust, wear-resistant composite ceramics;
- adsorbents, which generally consist of a carbon composite material and SiO_2 or activated carbon;
- adsorbents to purify waste waters and water basins from oil and oil products;
- mixed (C/SiO_2) or pure (C, SiO_2) fillers for thermoplastic polymers;
- potential source of renewable energy, non-pollutant to the environment;
- porous carbon materials, used as active materials in Electrochemical Current Sources (ECCS) and super capacitors;
- from composure perspective, rice husks could be used straight into metal processing for the production of iron – silicone alloys.

The presented possible approaches to utilise the rice husks, being the waste during the acquisition of the grain, layout the fundamental directions to turn a waste into a prosperous raw material to obtain carbohydrate-silicon containing high-tech material, usable in various areas.

The successful reuse of rice husks in industrial scale will also help solve the ecological problem, related to the accumulation, storage and management of this environment pollutant.

The utilisation, reuse and application of carbohydrate-silicon containing components, contained within the rice husks cold be done with the aid of innovative methods and technologies such as:

- with the use of thermochemical methods over composite C/SiO_2 materials with defined composition and structural characteristics;
- extraction of SiO_2 with alkaline-hydrothermal treatment of raw rice husks and optimisation of the Si extraction degree;
- synthesis of low-cinders porous carbon materials with the aid of pyrolysis and chemical activation of alkaline hydrolysis.

Figure 1 show a principal technological scheme to extract carbohydrate-silicon containing components from rice husks and the production of added value materials – active carbon – with high applicability across various technological domains.

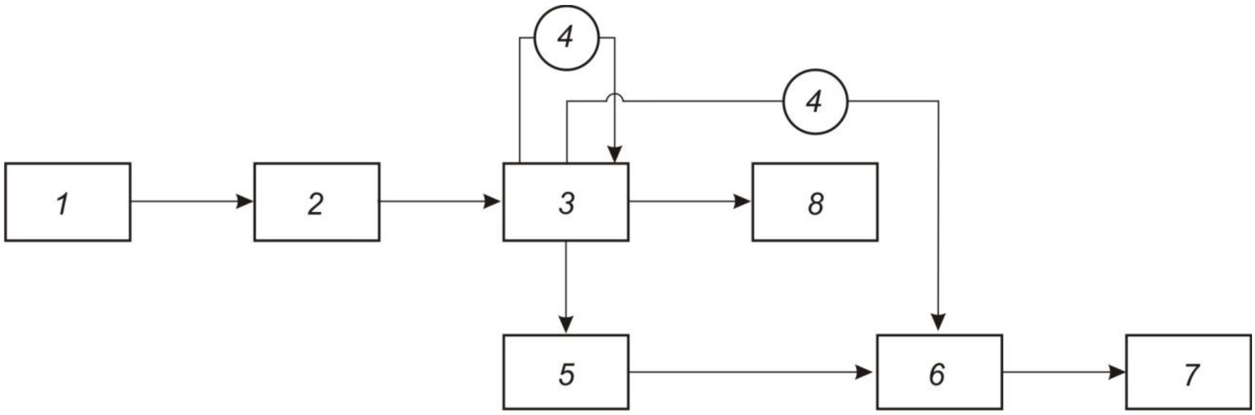

Fig. 1. Principal technological scheme to produce active carbon from rice waste:
1. Separation of the raw material (rice waste); 2. Hydro – preparation of the raw material; 3. Reactor to separate silicon components; 4. Pyrolysis gas input; 5. Filtration; 6. Carbon reactor; 7. Packaging of the end product (active carbon); 8. Packaging of secondary product (water glass)

CONCLUSIONS

The possibilities to obtain carbohydrate-silicon containing components from the composition of rice husks, as reviewed in this paper, present an ecological and resource optimised alternative to utilise part of the secondary (waste) products from rice production.

During the preparation of this paper, a detailed analysis of one of the primary sources of income for the Bulgarian – the rice production, was made. The sown areas and their distribution in territorial terms was also discussed with the averaged harvests, the soil-climate particularities and the infrastructural parameters of this branch.

With emphasis on the innovative thermochemical methods and technologies to extract and use the carbohydrate-silicon containing components, contained within rice husks, we have introduced the possibilities to apply the products of these processes;

The offered principal scheme to extract carbohydrate-silicon containing components from rice husks and the production of added value materials (in the present case – active carbon) with high applicability in different industrial domains.

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