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Research article

Production, Properties and Use of the Rice Hulls Pyrolysis Organic Product as a Disinfectant

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Abstract:

The article introduces the results of laboratory and field tests on production of the organic product (OP) of the rice hulls pyrolysis and data on the OP composition and biological activity. It was proved that a rise in the rice hulls pyrolysis temperature from 350°C to 650°C leads to an increase in the OP yield from 20% to 36% of the rice hulls weight. At that, the yield of sulfuric-ether fraction in OP increases from 10% to 45% and the yield of alcoholic fraction grows from 0.3% to 5%. At the optimum pyrolysis temperature (600-650°C) the composition of the sulfuric-ether fraction is as follows: phenols 18-20%, acids 45-47%, neutral substances 32-35%.It was proved that the organic product has a high bactericidal and fungicidal activity against various bacteria and mycotoxins and can be applied as an antibacterial agent and disinfectant. The effect of the OP aqueous solutions (6% to 100%) on the Mycobacterium phlei strain was studied. It was proved that solutions which contain more than 6% of the organic product have a high bactericidal activity against Mycobacterium phlei. The study of the disinfecting and corrosive characteristics of the 10% OP solution against Mycobacterium phlei on the test sheets made of wood, brick, concrete, rubber, steel and galvanized iron showed that the disinfection was complete and the corrosiveness of the solution was considerably lower than that of the standard 3% formaldehyde solution.
The new disinfectant has been patented in the Republic of Kazakhstan and recommended as a disinfectant in veterinary medicine.

Keywords: Rice hulls, organic product, disinfectant

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1 Introduction:

Rice hulls are a waste of the rice processing that almost is not in demand.

Global annual volume of the rice hulls formation is 150-200 million tons. In Kazakhstan, mostly in Kyzylorda oblast, it is produced up to 90 thousand tons per year.

The problem for the hulls utilization in the industrial environment is still not resolved. Rice hulls in limited quantities are used as a fuel, for abrasives and adsorbents producing, as an additive for building materials, in agriculture (as bedding for animals and feed additive), and as a source of silica and raw material for chemical recycling (SergiyenkoV.I., et al, 2004;Lathrop E.C., 1952; ChshibryaA.Yu., 2000;Nguyen TienHoa,2005; Zemnukhova L.A. et al, 1996) that is not always economically justified (Houston D.F., 1976).

Therefore more than half that quantity of the rice hulls doesn't finduse in the world and is sent to dumpsgenerating environmental problems

We have developed a technology for complex rice hull processing (Sukharnikov Yu.I., et al, 2012)to obtain two products: silicacarbon and organic product. The essence is that the rice hull is subjected to pyrolysis at the temperature 600-650°C for 20-30 minutes. The resulting product is a solid silicacarbonproduct that is a multifunctional material (Sukharnikov Yu.I., et al, 2009) and is used as fillerfor rubbers and carbon materials, sorbent and a feed additive in poultry.

Liquid organic product (OP) is an aqueous solution of aliphatic and aromatic hydrocarbons, which includes about 40% sulfuric-etherfraction and 35% neutral substances.Organic product has a high antimicrobial activity against staphylococci, streptococci, collibacillusand dysentery bacillus, salmonella, candida, and OP contains no benzopyrene, and therefore it does not have carcinogenic substances. According to the results of the National and Practical Centre for Sanitary and Epidemiological Expertise and Monitoring of the Ministry of Healthcare in the Republic of Kazakhstan, at intragastric introduction of OP refers to the 4th class of danger (low-risk) that can be recommended for the widespread use.

A pilot production has been created forprocessing 300 kg of the rice hulls per day to produce 100 kg silicacarbonand 75 kg organic product.

The following disinfectants are registered in the state register of Kazakhstan: Glyuteks (Spain), GAN (Russia), Rokal-20 (Kazakhstan), Bromodialon (Serbia and Montenegro), Deksid-200 (Netherlands), Povidone-iodine (China).

Based on the composition and properties of OP as well as the composition of the known disinfectants, OP must have a certain influence on the Mycobacterium phlei strain.
The object of this study is to obtain the organic product during thermal processing of the rice hulls under the pilot production, to study its chemical structure and biological activity, as well as to carry out the tests as an antiseptic substance and disinfectant in veterinary.

2 Main Part

2.1 Organic product at the pilot plant

The process of complex rice hulls processing is its thermaltreatment at the temperature600-650°C in the sealed unit.Thereby a solid silicacarbon product(C_{gen}: 48-53%, SiO_2: 37-40%, hydrocarbons:10-15%)and liquid organic product (aliphatic hydrocarbons: 45-55% aromatics: 22-28%, restH_2O) are formed. Performance of the pilot plant (Figure 1) is 300 kg of the rice hulls per day, plus 100 kg silicacarbon and 75 kg organic product, the rest is energy gas with a calorific value 2000-2500 kcal/kg.

Figure 1. Pilot plant for the rice hulls processing

The resulting organic product is packaged in containers of 5-10 liters and directed to research and testing as a disinfectant.

2.2 The study of the organic product composition and properties

OP is a brown, oily liquid, partially soluble in water, with a strong phenol smelllike a liquid smoke.

Aqueous solutions had strongly acidic reaction (pH = 4.0), produced intense brown staining with ferric chloride (Fe^{+++}), and in the ultraviolet spectra there were absorption maximums λ- 20.6, 22.0, 278 nm, indicating the presence of phenols.
OP was highly soluble in alcohol and partially in ether.
In order to determine the chemical composition, the OP was subjected to the separation for ether-, alcohol-soluble, phenolic, acidic and neutral fractions. It wasfound that, depending on the temperature of pyrolysis the output of OP and the ratio of its components are changed over a wide range, as there is the evidence from the results shown in Table 1.

Table 1. Output and composition of the products according to the pyrolysis temperature

Pyrolysistemperature, °C	Condensate output, % of rice hulls	Fraction output, % of condensate		Fractionoutput, in % of sulfuric ether fraction		
		sulphuricether	alcohol	phenolic	acidic	neutrals
300	12	4.0	0.1	5.0	49	20
350	20	10.2	0.3	10.0	48	22
400	22	39.1	0.4	15.0	47	25
500	35	41.1	0.5	19.0	43	38
800	30	24.5	11.0	15.0	46	29

This Table shows that increasing pyrolysis temperature to 500°C the output of OP and its content of phenols and neutrals is going to increase, whereas the output of acidic fraction is practically unchanged. When increasing pyrolysis temperatures up to 800°C, there is a decrease at the overall outputof OP and contentof phenols and neutrals in it.
All fractions derived from OP were tested for antimicrobial effect. Studies were carried out by the method of serial dilutions on a liquid nutrientin a wide range of doses from 5000 to 10 µg/ml.

The study results showed that the phenols, acids and alcohol fraction have bactericidal and fungicidal activity. The most active fraction is phenol fraction (39 µg/ml), then alcohol-soluble substance (78-156 µg/ml) and less likely acid one (156 µg/ml).

Thus, the OP has a broad spectrum of antimicrobial activity and can be used as a bactericidal and antiseptic agent.

As the greatest activity was observed in phenol fractions, it was primarily subjected to in-depth chemical study. OP fractions had been studied. They were obtained at pyrolysis temperatures 500°C and 800°C. Such fractions were analysed by gas-liquid chromatography (GLC).Chromatography was conducted on Byrukhrom chromatograph with a flame-ionization detector, the phase - 15% polyethyleneglycolsuccinateat Chromaton N-AW (0.2-0.25 mm), column temperature - 180°C evaporator temperature 250°C gas-carrier pressure 1.2 kg /cm.The fraction qualitative composition was determined by the taps on the retention time, the quantitative one –by the method of internal normalization. Acids were chromatographed as their methyl ethers.
Phenolscomposition and their number changing in OP depending on the rice hulls pyrolysis temperature are shown in Table 2 (substances are listed by their output from the column, by retention time).

The presence of 13 components was established in the phenolic fraction. Mains among them were phenol, meta- and para-cresols, creosol and 2 unidentified phenols. These components were 85% of the phenolic fraction obtained at 500°C and 83% at 800°C. The other components: methyl and propylcreosol, methylguaiacoland othersare only in small amounts.

The GLC results showed that pyrolysis temperature increasing significantly affects not only the phenol outputs but also their composition.

Table 2. Phenol composition depending on pyrolysis temperature

PeakNoin chromatogram	Component name	Compositionin% of the phenolic fraction	
		pyrolysis temperature 500°C	pyrolysis temperature 800°C
1	X 1	3.2	2.3
2	Creosol	9.7	4.7
3	Methylcreosol	4.3	2.4
4	Propylcreosol	4.6	3.2
5	X 2	10.4	1.8
6	X 3	13.9	14.4
7	Phenol	17.0	31.2
8	0-creosol	8.7	11.7
9	M- и p-cresjol	13.6	19.0
10	Guaiacol	12.5	7.2
11	Methylguaiacol	0.9	0.7
12	X 4	0.5	-
13	X 5	0.7	1.4

The phenol fraction derived from the OP at pyrolysis temperature 800°C, the amount of phenol, o-, m- and p-cresols significantly (at 22.6%) increases and at about the same amount the content of guaiacol, creosol, unidentified component X_2 is reduced. The findings suggest that increasing temperature pyrolysis of the rice hulls the degree of demethylation of formed phenols is increased too. Indirectly this indicates that the unidentified components X_1, X_2, X_3 are methylated phenols.

OP acidic fraction obtained by pyrolysis temperature 500°C and 800°C was studied by GLC at the same plant under similar conditions. The results are shown in Table 3.

Table3. Acidic fractionscomposition depending on pyrolysis temperature

PeakNoin chromatogram	Acid name	Output of the total acid, %	
		pyrolysis temperature 500°C	pyrolysis temperature 800°C
1	Propionic	0.8	1.2
2	Oil	2.0	1.4
3	Isovaleric	5.3	1.9
4	Benzoic	4.5	1.5
5	N-Valeric	3.8	1.1
6	Caproic	5.3	1.6

7	Salicylic	5.6	1.7
8	Enanthic	3.1	0.9
9	X_1	3.4	0.5
10	Caprylic	3.3	1.1
11	Veratric	2.3	0.6
12	Cinnamic	24.9	3.6
13	Vanillin	2.2	0.6
14	Terephthalic	0.9	0.6
15	Ferulic	4.5	1.4
16	Protocatechuic	19.6	1.7
17	P-hydroxybenzoic	7.8	05
18	β-resorcylic	0.6	57.6
19	γ - resorcylic	0.1	20.5

As it is seen from the data given,the main components of acid fraction (500°C) are cinnamic, protocatechuic, p-hydroxybenzoic, salicylic, caproicand isovaleric acids, which accounted for 68.5% of the total amount.

With increasing pyrolysis temperature up to 800°C, the content of β and γ resorcylic acid rapidlyincreases, whereas the amount of cinnamic, protocatechuic and p-hydroxybenzoic, salicylic, veratric is greatly reduced.

The OP studied has a composition of phenolic and acid fractions, similar to the composition of lignin pyrolysateof hardwood(Liverovskiy A.A., et al, 1967).

Organic products of pyrolysis of the rice and cotton hulls, which contain phenol, cresol, guaiacol can be used as an insecticide and bactericide (GoryayevM.I., et al, 1969). Phenol, cresol, guaiacol are also included in the liquid smoke.

It is very significant that it does not contain benzopyrene of carcinogenic substances. UV and IR-spectras of OP showed no peaks (λ = 225, 254, 265, 274, 284, 296, 347, 363, 384, 403 nm) that is characteristic for benzopyrene.

The greatest output of OP and its phenolic fraction is observed at pyrolysis temperature 550-650°C, which is accepted as the optimum one.

Taking into account such OP properties it can be widely used in agriculture, medicine and other industries.

2.3 The use of the organic product of the rice hulls pyrolysis for animal feed treatment

For experiments on the ducklings,5 groups by 50heads were chosen.

The first group of ducks received a standard feed (control). The second one got the same feed but mixed with OP at the rate of 2 ml per 1 kg of feed. Feed for the third group of ducklings wastreated at the rate of 4 mlof OPper 1 kg. As for the forth group, 6 ml of OP were added to the feed, and for the fifth one - 8 ml per 1 kg of feed.

The experimental results are shown in Table 4.

Table 4. Keyzootechnic indicators for ducklings which received feed treated with a solution of OP.

Indicators	Groups				
	1 (c)	2	3	4	5
1. Live weight of ducklings at day old, grams	51	50	51	52	52
2. Live weight at week old, grams	175	172	178	172	188
3. Live weight at three weeks old, grams	870	898	914	919	988
4. Live weight gain for 1-21 day, grams	819	848	863	867	932

5. Food consumption per group, kg	138	124	124	130	130
6. Food consumption per 1 head for 1-21 day, kg	2.75	2.48	2.48	2.60	2.60
7. Feed-use efficiencyper 1 kg of live weight gain, kg	3.36	2.87	2.87	3.0	2.8

With the absolute preservation of livestock in such experiment, different results were given for live weight gain and feed-use efficiency. They turned out to be the most revealing in the fifth group, in which the feed was processed at the rate of 8 ml of OP per1 kg of feed.

It gives the following evidence: feed treatment with OP solution made a significant influence on the decreasing of general microflora of the feed infected by toxicants.

The content of erythrocytes, hemoglobin and total protein in blood of the ducklings of this group wasthe greatest. All this indicates the removal of the negative impact of mycotoxins on digestion and the acceleration of growth and live weightgain.

2.4 Organic product study and testing in veterinary

The OP disinfectant properties were studied at the test objects of different materials: wood, brick, concrete, galvanized and typicaliron plate, sandstone plateand rubber. The surfaces of the test objects were contaminated with one billionth of M. phlei suspension at the rate of 1 cm^3 per 10 cm^2. Then the test objects were treated with the test10% solution from the hand-operated sprayerat the rate of 1 liter per 1 m^2. The exposure time was 60 minutes.

In 60 minutes there were disposals from the test objects which were washed by centrifugation at 3000 rpm three times with sterile saline. Seeding was made from the precipitates on Lowenstein-Jensen by 5 vials from each sample and thermostated at 37°C for 15 days. The results are given in Table 5.

Table 5. Disinfecting properties of the test product of the rice hulls pyrolysis

Materialtype (testobject)	M. Phleigrowth presence	
	10% solutionof OP	Sterilesaline - control
Wood	-	+
Concrete	-	+
Rubber	-	+
Metal	-	+
Brick	-	+
Plate	-	+

The data in Table 5 shows that 10% solution of OP at a rate of 1 liter/m^2 and exposure for 1 hour provides a complete disinfection of surfaces tested from mycobacteria. There was no M. phlei growth in all tubes of Lowenstein-Jensen environment during the period of observation (15 days), at the same time in the control M. phlei there was growth in 7 days at the nutrient.

OP corrosion properties were tested for steel (grade 3 and 45), for aluminum alloy (grade AMG-b and AMG-8) and for galvanized iron.

Corrosivity was determined during the test by reduction in the samples weight (test plates). Experiments were carried out with the full immersion of the test objectsto 10% solution at ambient temperature for 150 hours. For a control they used 3% solution of formaldehyde as a widely used disinfectant for livestock farms (Table 6).

Table 6.OP corrosivity

Preparatios	Materials	Mass, g		Massloss	
		before	after	g	%
10% solutionof OP	Steel-3	6.8100	6.8086	0.0014	0.018
	Steel-45	7.6350	7.6350	0	0

	Duraluminum(AMG-b)	6.5209	6.5183	0.0026	0.041
	Duraluminum(AMG-8)	6.3483	6.3464	0.0019	0.028
	Galvanizediron	8.0024	8,0008	0.0016	0.022
3% solutionofformaldehyde	Steel-3	7.7072	7.7050	0.0022	0.028
	Steel-45	8.6010	8.6000	0.0010	0.011
	Duraluminum (AMG-b)	6.2834	6.3793	0.0041	0.064
	Duraluminum (AMG-8)	6.3180	6.3148	0.0032	0.049
	Galvanizediron	6.7780	6.7753	0.0027	0.038

Analysis for the preparations corrosivity according to the digital data in Table 6 shows that the organic product of the rice hulls pyrolysis substantially has less corrosive activity compared with 3% solution of formaldehyde. OP in 10% concentration regarding Steel-45 showed no corrosive activity, whereas treatment with formalin corrosive activity for 1% of its concentration amounted to 0.8 g /m^2 and for 3% = 1.6 g/m^2. For the other, used in the study of metal samples, there is apresence of low OP corrosivity.

Thus due to the results of the studies carried out it was found that 10% OP has bactericidal, bacteriostatic activity towards M. phlei, has low corrosiveness against metal objects and can be used for disinfection in tuberculosis.

Production and laboratory testing for disinfection was conducted by “Rishel” preparation (commercial name of a new disinfectant based on OP) on objects contaminated with Mycobacterium tuberculosis in the vivarium of TB laboratory atthe Kazakh Scientific Research Veterinary Institute. The vivarium contained imported from “Zhaksylyk” economic entity 15 calves infected subcutaneously with 1.0 cm^3 suspension of a virulent culture of Mycobacterium ofM. bovis-8 bovine species at the rate of 5 mg per animal. After the end of the experiment the animals were killed and dissected for veterinary-sanitary research and for selection of the biological material samples for microbiological examination.The premises were treated with the test 10% solution from the hand-operated sprayerat the rate of 1 liter per 1 m^2. Exposure time was 180 minutes.

Surfaces of the premises wereirrigated with disinfectant solution in the following order: first, starting from the end of the premise near to the entrance, equally moistened floorand then the ceiling. At the sametime theydisinfected the objects of care for the animals and equipment used in this area.
After the completion of disinfection, the vivarium premises were sealed (doors and windows) and left for 3 hours. After exposure for 3 hoursthey did washings of the test objects with sterile tamponstothe sterile tubes with tap water. The contents were transferred to centrifuge tubes; the pre-seeding treatment was carried out with 6% solution of sulphuric acid; and they were centrifuged for 20 minutes at 3000 rpm. Then they were washed with sterile saline and centrifuged twice. From the centrifugate the seeding was made to Lowenstein-Jensen nutrients and thermostated at 37°C for 30 days. The seeding was carried out also from the control test objects, treated instead of disinfectant with sterile water.

It was found out that the 10% solution of OP at the rate of 1 liter/m^2 and exposition for 3 hours provides a complete disinfection of surfaces from mycobacteria. And there was no mycobacteria growth during the period of observation (30 days) in all tubes of Lowenstein-Jensennutrients. At the same time there was a growth at the control in the nutrientsin 5 days.

Performance test of the organic product as a disinfectant was made at the “Shokan& Co” farm,where were also identified the cases of allocation of animals reacting to tuberculin. Spraying with 10% solution of the preparation was carried from the towing equipment to thewheel-type tractor at the rate of 1 liter/m^2 on the farm area about 1,000 m^2, which contained 300 heads of cattle. The test objects washes (ceramic plate, concrete and wood surfaces) were taken to the tuberculosis laboratory after the exposure for 3 hours, where the bactericidal effect of the preparation tested was set by the bacteriological examination in terms ofthe culture tested - M. phlei.

The normative and technical documentation for the tested preparation is ready. The organization standard was examined and approved by the Committee for Veterinary Control and Supervision of the Ministry of Agriculture of the Republic of Kazakhstan.

The preparation has a bactericidal, bacteriostatic (gram-positive and gram-negative bacteria), fungicidal and antiviral properties regardless of humidity, ambient temperature and is readily soluble in water. It is possible to use the preparation in the presence of animals or birds. The patent of the Republic of Kazakhstan was received for this preparation.

The proposed disinfectant is recommended to disinfectlivestock premisestroubledby tuberculosis and other objects of veterinary supervision.

The “Rishel-plus” preparation with various OP concentrations and little addition of technical sulphuric acid and chloride alkyldimethylbenzylammonium (katsell) was developed to reduce OP concentration in the solution for disinfection. Disinfection conducted by this preparation according to the methodological guidelines “On Procedurefor Testing New Disinfectants in Veterinary Practice”at the“Nurgozha”livestock enterpriseshowed thatthe stimulated (current and final) disinfection of surfaces by the veterinary supervision in the farms, troubled due to tuberculosis, can be carried out withthe “Rishel-plus” preparation" with 5-6% concentration for wet disinfection at the rate of 1 liter/m^2 and exposure time for 3 hours.

3 Conclusion

The technology has been developed and the pilot productionforthecomplex rice hulls processing has been created to produce silicacarbon and organic product.The silicacarbon is a polyfunctional product and can be used as filler for elastomers and carbon materials, a sorbent, charge material for melting silicon and special silicon ferroalloys, as well as a feed additive in poultry and livestock.

The organic product is an aqueous solution of aliphatic (45-55%) and aromatic (22-28%) hydrocarbons, in composition of which there are 35% neutrals and 40% sulphuric-etherfraction whose output at the optimum pyrolysis temperature of the rice hulls (600-650 °C) is 38-42%. Its composition isas follows: 18-20% phenolsand 43-46% acids.The full composition of phenols (13 names) and acids (10 names) is identified. The organic product has an expressed bactericidal and fungicidal activity against streptococci, staphylococci, collibacillus, dysentery and tubercula bacillus, salmonella, candida. It contains no benzopyrene, and therefore can be used for disinfection of feed and livestock premises. The research results and pilot testing showed its high disinfecting effect.

The disinfection agent based on 5-10% solution of the organic product of the rice hulls pyrolysis has beendeveloped and recommendedfor practical use.

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