

UDC 575.21: 633.15
Original scientific paper

A GENETIC BASE OF UTILISATION OF MAIZE COB AS A VALUABLE NATURALLY RENEWABLE RAW MATERIAL

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Božović I., M. Radosavljević, S. Žilić, R. Jovanović (2004): *A genetic base of utilisation of maize cob as a valuable naturally renewable raw material.* – Genetika, Vol. 36, No. 3, 245-256.

The original technological method of the maize cob processing has been developed at the Maize Research Institute, Zemun Polje, by which lignocellulose granules of different particle sizes are produced from the cob. Different chemical composition and physical and chemical properties of these fractions, and especially a great capacity of binding liquids, particularly oil and water determine, their usage as degreasing and drying means. Due to their great hardness and abrasive capacity, products made from ground cobs are usable for polishing in the metal processing industry, while the composition of certain compounds (pentosan) are of a particular importance in the chemical industry for the production of furfural and its derivatives. As these products are inert, of neutral pH and free of heavy metals they are used as organic carriers in the production of pesticides and agro-chemicals, as well as, in cosmetics and the pharmaceutical industry.

Key words: maize cob, lignocellulose granule, celgran products, absorption, degradability, utility value

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INTRODUCTION

The maize cob is a very important by-product in the maize grain production. Approximately 180 to 200 kg of cobs are produced per tone of grain. The annual production of this secondary raw material amounts to 1.2 to 1.5 M tons in our country. The conventional application of the cob in agriculture as fuel or coarse fibre feed is also expanded to the industry.

The highest amount of cobs used in the industrial processing in the world is used in the chemical industry for the production of furfural, while the remainder after its separation (compounds encompassing degraded parts of cellulose) is used as a specific feed or for the production of activated coal. There have been attempts to produce the following products by the cob industrial processing: acetic acid, methanol, charcoal, xylitol, furfural, etc.

The cob chemical composition and particularly its physical and chemical properties (degradability, absorption), then neutral pH, absence of resins and waxes, as well as, a crucial fact that heavy metals are present either in negligible amounts or there is not even a possibility of their detection, make the cob an ideal organic carrier. It is an ideal carrier for micro ingredients, for feed, first of all for the greatest number of vitamins, then in the pharmaceutical industry - a carrier for antibiotics, in cosmetics - a carrier for deodorants, etc. However, the initial raw material for the industrial processing, as well as, for other purposes requires its physical adaptation, i.e. its mechanical pulverisation, pelleting and air separation. Such produced cellulose granules arise a great interest in the metal processing industry as means for degreasing, drying and polishing, as well as, for cleaning surfaces of spilled crude and fuel oil, BEKRIĆ *et al.*, 2000.

THE COB MORPHOLOGICAL STRUCTURE

The maize cob is the elongated woody core of the ear with a physiological function to provide photosynthetic compounds and water to the developing grains. There are three prominent zones in the cob cross-section: central, placed in the centre of the spindle, that makes a core, then the zone of woody cylinder and the peripheral layer that encompasses the layer of coarse and the layer of fine glumes.

A woody cylinder with a core fulfilled with soft parenchyma consists of a mighty conductive system that is accompanied by the complex system of sclerenchyma and woody parenchyma throughout the ear. In the process of drying the parenchyma reduces and the dry cob is very often spongy. The tissue hardness of the woody cob is four fold greater than the hardness of the maple wood. This property, as well as, the fact that it does not encompass resins, waxes or free acids make it usable for many purposes, BEKRIĆ *et al.*, 1998. A morphological structure is very important for the cob as a raw material. Table 1 presents the composition of certain morphological fractions of cobs of twenty seven different ZP maize hybrids.

Table 1. Composition of certain morphological fractions of cobs of twenty seven different ZP maize hybrids

Hybrid	Glume (%)	Woody part and grain clippings (%)	Core (%)
ZP 42a	9.37	89.01	1.62
ZP 243	8.55	90.20	1.25
ZP 300b	3.40	95.34	1.26
ZP 360	5.52	92.63	1.85
ZP 434	10.66	87.47	1.86
ZP 480	6.61	91.84	1.55
ZP 488	6.79	92.14	1.07
ZP 511	7.26	91.74	1.00
ZP 539	9.77	88.88	1.35
ZP 551b	5.15	93.73	1.12
ZP 570	6.92	91.53	1.55
ZP 580	4.93	93.92	1.15
ZP 599	7.41	91.31	1.28
ZP 633	8.25	89.94	1.81
ZP 677	7.21	91.38	1.41
ZP 680	6.49	92.37	1.14
ZP 684	4.64	94.24	1.12
ZP 702u	7.58	90.54	1.88
ZP 703u	14.94	83.14	1.92
ZP 704	9.34	89.25	1.41
ZP 704nu	8.65	89.90	1.45
ZP 709t	7.37	90.94	1.69
ZP 735	8.56	89.70	1.74
ZP 737	7.47	91.00	1.53
ZP 750	8.38	90.16	1.46
ZP 753	6.66	91.96	1.38
ZP 808	5.42	93.41	1.17

THE COB UTILISATION

In agriculture the cob is conventionally used as feed, litter, a medium for the mushrooms cultivation, a carrier for seed and similar. The utilisation of the cob as fuel, coarse cellulose feed, litter, has evolved into the production of carriers for feed micro ingredients. Being of neutral pH, with no resins and waxes, the cob granule is compatible with the majority of vitamins and other additives, hence it is almost a perfect organic carrier for feed micro ingredients, BAGBY and WIDSTROM, 1987.

Cob meal as an organic filler. Due to the fact that it does not encompass acids, resins and waxes, and that it does not reduce viscosity of fluids, cob meals can be used as carriers for pesticides, insecticides and premixes - both, vitamin and mineral ones. Their advantages over mineral carriers lays in the fact that they readily release chemicals and once incorporated in the soil they will biologically degrade in time not disturbing the soil structure, ARONOVSKY *et al.*, 1950.

A cob soft fraction is used for making granules that are used in the production of the compost - a medium for the mushroom cultivation. When 10-20% of cellulose pellets were added to horse manure costs of both, transport and mushrooms cultivation were reduced and also the time for compost warming was shortened. In a similar way, pellets added to litters showed a high capacity of urine and dung absorption contributing to faster bedding airing. There is a demand for granules as a mean for the reduction of the control medium circulation in oil drilling with mechanical augers. Therefore, the use of cob products is broad and it is permanently broadening.

Cob soft-grit or maize-absorbent is widely used from the cleaners of carpets, furs to great electric isolators in distributive substations of uninterrupted power supply, then from cleaning carbon deposits in inner combustion engines and boilers for natural gas/heavy fuel oil combustion to the production of cosmetic preparations, VANDER HOOVEN, 1973.

The absorbent for removing oil spilled on the surface of open waters is made out of light fractions of "alive floating cob granules". It is not harmful to water plants and animals. It is sprayed over spilled layers of oil and pumped out with pumps. It can absorb crude oil five times its weight, so it means that 250 kg of this absorbent can absorb one tone of spilled crude oil.

Grit absorbent in the metal industry. An appropriate granulation of air separated ground cobs is an ideal abrasive and absorptive medium for fine polishing of metal surfaces. Its effect of polishing and cleaning with a shorter operating time of the machine is much better than the effect produced by similar wood products.

Soft cob grit is an efficient mean for the removal of lime deposits in boilers, carbon deposits in inner combustion engines and a very successful cleaner of large isolators on long-distance power lines. A high absorptive capacity, slight abrasiveness and non-adhesiveness of some granulations provide efficient cleaning and polishing of platinum products.

Cellulose grit as an additive for casting sand. Cob grit of a certain granulation was tested as an additive in casting sand. Due to its pulverisation it creates an air bag during casting. After cast injection particles readily combust outside of the core and then are easily shaken out, while the cast remains with a formed surface of high quality.

COB PROCESSING

Unique physical and chemical properties of the cob among other plant materials attracted a great attention of researches in the 1950's. However, as early as the 1930's, the attempts were made to industrially produce acetic acid, methanol, charcoal, xylitol by the destructive distillation out of the xylan in which the cob is rich. Furfural is a product with a permanent place in the chemical industry and if the demands for it continue to rise by the today's rate the increase of the production will have to be provided from plant raw materials as it is not possible from minerals anymore. In Europe, furfural is mainly produced from the cob. The leftovers in

the furfural production make over 70% of the initial material and they are a mass with components of degraded cellulose and although without values for the fuel the remaining material can be used as feed or in the production of activated carbon, FOLEY and VANDER HOOVEN, 1981.

The processes of producing generator gas by cob combustion in the compacted layer with the limiting air intake attracted a great attention at one time. The produced gas approximately consists of 30% carbon monoxide, 10% hydrogen and 50% nitrogen, while the rest, consists of carbon dioxide and methane. It was used as fuel for inner combustion engines or for air warming for maize drying. The USDA Agency for Agriculture and Industrial Chemistry developed synthetic liquid fuel from the cob, BEKRIĆ, 1997.

Furthermore, in contrast to chemical cob processing, there is a great interest and demands for cellulose granules mechanically produced from cobs. Unique physical and chemical properties, first of all pH and hardness, provided the development of the products in two directions. The first one is producing granules for cleaning, polishing and drying in the metal processing industry (the production of ball bearings, jewellery, bijouterie, gears and other products). The second direction is producing of organic carriers for chemical industry, especially for the industry of agrochemicals.

Processing of cobs for different purposes is very complex. Some manufacturers claim that it is more expensive to ground a tone of cobs (due to great hardness) than a tone of extremely hard iron ore. The cob is so abrasive that wears out working parts of grinding machines, even metal, stainless steel mesh screens. It is also known that it is not easy to store the cob, as if wet rapidly mildews and gradually rots and very often spontaneously inflames developing wet, pernicious sweet odour. Ground particles are dry and there is a risk of explosion at manipulations with them. Due to stated problems, many systems of the milling equipment were tested and a lot of them proved to be inefficient. The general theoretical assumption is that mechanical pulverisation, air separation and granulation are to be done by a series of masher-crusher and hammer mills up to the desired particle size, BEKRIĆ *et al.*, 2000.

According to the original technological design the cob processing pilot plant was installed at the Maize Research Institute, Zemun Polje (BEKRIĆ *et al.*, 1998).

Processing is proceeded in several stages:

- Pre-milling - coarse crushing;
- Separation - crushed material is separated on the air separator into two fractions - hard or woody fraction which mainly represents a broken woody part of the cob and a soft or chaffy fraction which consists of glumes, core, grain clippings and fine dust;
- pulverisation - in order to obtain final products of certain properties, a hard fraction is further pulverised and passed through smaller-hole screens;

- granulating - the pulverised material of the hard fraction is conducted over the air separator to vibration screening.

The capacity of this experimental plant amounts to 420,000 kg of processed cobs.

PRODUCTS MADE FROM THE COB

According to the original ZP technology of the cob processing lingo-cellulose granules - CELGRAN products are produced. These products are intended for the metal processing industry and the chemical industry and cannot be found on the local market, RADOSAVLJEVIĆ *et al.*, 2002.

The following granules were produced in the designed pilot plant:

CELGRAN A - granules that pass through 3-mm sieve

CELGRAN B - granules that pass through 2-mm sieve

CELGRAN C - granules that pass through 1-mm sieve

The final CELGRAN products are successfully applied as:

- means for efficient degreasing, drying and polishing in the metal processing industry and the electric industry;
- organic carriers of high performances efficiently used in the production of pesticides and agrochemicals in the pharmaceutical industry and cosmetics;
- means to separate heavy metals from liquids and to wash water, i.e. to remove oil stains from open water surfaces by which ecological disasters are mitigated.

CHEMICAL COMPOSITION AND PHYSICAL AND CHEMICAL PROPERTIES OF CELGRAN PRODUCTS

The dominant part of a tissue of a mature cob consists of cellulose, pectin substances and mineral particles incrustated by lignin. These compounds provide compact-hard consistence of cell walls encircling and making a woody cylinder. A lignocellulose complex is the most important component of the chemical composition and according to GOLIK (1961) it makes at least one third of the cob dry matter.

Cob fractions separated by layers differ by their physical and chemical traits that define their functional properties which many technologists consider unique, FOLEY, 1978.

Results on determination of the basic chemical and lignocellulose composition of ZP maize cob products are presented in Tables 1 and 2 (BOŽOVIĆ *et al.*, 2003). Based on its basic chemical composition lignocellulose granules, i.e. CELGRAN A and B fractions of the maize cob do not differ from one another. The oil content was very low in these fractions and amounted on the average to 0.38%, while it was seven fold higher in the fraction C and amounted to 2.74%. The ash content was low in all three fractions, but according to the statistical analysis it was significantly lower in the fraction B than in other two fractions. Although low, the

protein content in the fraction C was higher by 42% than in fractions A and B and amounted to 3.92%.

Table 1. Basic chemical composition of CELGRAN products

Celgran product	Dry Matter (%)	Proteins (%)	Oil (%)	Ash (%)
A	95.30 ^b	2.31 ^b	0.40 ^b	1.61 ^a
B	98.12 ^a	2.23 ^b	0.37 ^b	1.21 ^b
C	95.41 ^b	3.92 ^a	2.74 ^a	1.51 ^a
LSD _{0.05}	0.14	0.19	0.43	0.14
CV (%)	0.01	2.96	8.55	1.13

CV-coefficient of variation

A lignocellulose complex is made of the group of the following compounds: cellulose, hemicellulose, hexoses, pectins and lignin. The results of studies on the lignocellulose compositions indicate that the content of cellulose, ADF and NDF was the lowest in the fraction C, as well as, that there were no statistically significant differences in the content of hemicellulose and ADL among the observed fractions of CELGRAN products. The cellulose content ranged from 36.41% in the fraction C to 41.55% in the fraction A, while the hemicellulose content varied from 40.53% in the fraction C to 41.59% in the fraction A.

The fractions A and B are exclusively made of a woody part of the maize cob, hence it is quite understandable that they are of almost identical chemical composition. The fraction C is partially made of the cob core and the glumes that have a particular physiological role during the maize plant growth and development, hence it differs from the woody part of the cob by the type of the tissues which significantly reflects on the chemical composition of this fraction.

Table 2. Lignocellulose content of CELGRAN products

<i>Table 2.</i> <i>Lignocellulose</i> <i>content of</i> <i>CELGRAN</i> <i>products</i>	Cellulose (%)	Hemicellulose (%)	ADF (%)	NDF (%)	ADL (%)
Celgran product					
A	41.55 ^a	41.59 ^a	45.77 ^a	87.37 ^a	4.22 ^a
B	41.38 ^a	41.51 ^a	45.70 ^a	87.22 ^a	4.32 ^a
C	36.41 ^b	40.53 ^a	40.96 ^b	81.49 ^b	4.55 ^a
LSD _{0.05}	0.75	1.52	1.07	0.47	0.56
CV (%)	0.31	0.86	0.56	0.13	2.96

CV-coefficient of variation, ADF-acid detergent fibre, NDF-neutral detergent fibre, ADL-lignin

The fractions of CELGRAN A, B and C significantly differ in physical and chemical properties which define their purpose.

All three observed fractions show the greatest solubility in 1% sodium hydroxide. The solubility varies from 9.56 to 25.96%. The lowest solubility is detected in ethanol. The solubility of CELGRAN products in all solvents increased with the decreasing of granule sizes. The highest increase of the solubility (1:5) was found in acetone between fractions A and C (Table 3).

Table 3. Solubility of CELGRAN products

Solvents	CELGRAN products			LSD 0.01
	A	B	C	
Water	4.34 ^c	5.00 ^b	11.15 ^a	0.314
Ethanol	1.35 ^b	1.46 ^b	5.00 ^a	0.314
Acetone	2.19 ^c	4.96 ^b	10.99 ^a	0.314
Sodium hydroxide	9.56 ^c	11.99 ^b	25.96 ^a	0.314

All three fractions are characterised with a great water absorption capacity, but this capacity statistically significantly differed among fractions, especially between A and C. The absorption capacity of edible oil is significantly lower, but it increases 2.5 to 5 times with the increase of the moisture percentage in the material, which points out to a high correlation between water absorption and edible oil absorption after water absorption by a dry sample that amounts to $r = 0.992$ on which their utility value is based upon.

The data presented in Table 4 indicate that observed fractions absorb water more strongly than edible oil and that the absorption capacity of edible oil by the water saturated material is lower. There is a statistically significant difference in the absorption capacity among fractions. The smallest fraction absorbs five, *i.e.* four times more water, *i.e.* edible oil, respectively, than the fraction with the largest granules. The absorption of edible oil by the water saturated sample does not significantly differ from the absorption of edible oil by the dry sample in the fraction A, while the absorption capacity by the wet sample of the smallest fraction is five times lower than the capacity by the dry sample. It is quite understandable that many purposes of these granules are based on the water and oil absorption capacities, especially when these granules are used as means for degreasing, drying and polishing in the metal processing industry or in "washing" of water surfaces covered by spilled crude or fuel oil, BEKRIĆ *et al.*, 2000a.

Table 4. Water and edible oil absorption by CELGRAN products

Fractions	A	B	C	LSD 0.01
Water	108.90 ^c	156.40 ^b	580.16 ^a	24.64
Edible oil	30.38 ^c	79.50 ^b	129.27 ^a	0.623
Oil after water absorption (by a wet sample)	25.79 ^b	37.11 ^a	24.79 ^c	0.314
Oil after water absorption	118.08 ^a	220.18 ^b	286.22 ^c	0.314

(by a dry sample)

Based on the obtained results, the highest absorption capacity of crude oil was detected in the smallest CELGRAN fraction C, while the lowest absorption capacity was recorded in the greatest fraction A (Table 5). After 2h of CELGRAN soaking, the fraction C and the fraction A absorbed 255.51% and 102.19% of crude oil, respectively, i.e. 2.5 and 1 times the initial weight of the dry fraction, respectively. It was also observed that the absorption capacity of the fraction A gradually and statistically significantly increased with the prolongation of absorption time, hence after six hours it amounted to 121.40%, which is higher by approximately 20% in relation to the percentage of absorption after two hours. The saturation of the CELGRAN fraction B occurred after two hours, hence the absorption capacities of crude oil after two, four and six hours did not significantly differ from one another. The CELGRAN fraction C had the highest absorption capacity after four hours of soaking in crude oil and amounted to 283.25%, which means the fraction C absorbed crude oil three times its initial weight. Approximately 300 kg of the CELGRAN fraction C is necessary to remove one ton of crude oil spilled over water surfaces.

After 70 hours of drying of previously used fractions of the CELGRAN product soaked in crude oil for two hours, the percentage of remaining crude oil amounted to 38.61%, 31.45% and 19.14% in the fractions A, B and C, respectively, in relation to totally absorbed crude oil. Crude oil remaining in used CELGRAN products increases their caloric value, thus they can be used as fuel of a high energetic value. Furthermore, used CELGRAN products can be re-used for absorbing of spilled crude oil. Obtained results point out that the already used fraction A had the lowest absorption capacity (58.83%), while the absorption capacity of the used fraction C was higher than the absorption capacities of fresh fractions A and B used for the first time and amounted to 145.47% (Table 5).

Table 5. Crude oil absorption by CELGRAN products

Celgran product	2 hours (%)	4 hours (%)	6 hours (%)	2 hours for the second time (%)
A	102.19 ^g	110.57 ^f	121.40 ^e	58.83 ⁱ
B	127.96 ^d	126.76 ^d	127.28 ^d	65.20 ^h
C	255.51 ^b	283.25 ^a	282.93 ^a	145.47 ^c
LSD _{0.05}	1.70			
CV (%)	1.11			

CV-coefficient of variation

The determination of the binding capacity of engine oil by the fractions of CELGRAN products is very difficult. Considering the density of engine oil, it is known that the minor part of oil is absorbed, while the greatest part of oil remains on the surface of the granules of the observed products (*i.e.* the greatest part is adsorbed) providing its efficient removal from the water and other surfaces. The results presented in Table 6 show that the binding capacity of the fraction B was

lower by approximately 3% than the binding capacity of crude oil. On the other hand, the absorption capacity of the fraction C was higher by approximately 48% in relation to the crude oil absorption capacity of this fraction (RADOSAVLJEVIĆ *et al.*, 2003). The absorption capacity and adsorption of engine oil by the fraction A was approximately equal to the percent of the crude oil absorption by this fraction after two hours and amounted to 102.12% in relation to the weight of the initial sample.

Fractions of the CELGRAN products mainly bind fuel oil on the surface of their granules due to which a dense, compact layer is formed on the water surface over which fuel oil has been spilled and this layer prevents breakage and spreading of the spilled stain. The smallest fraction C absorbed the greatest amount of fuel oil, i.e. 213.16% the initial amount of the observed fraction, i.e. the total amount of spilled fuel oil (100%). The absorption capacity of the fraction A was the lowest and amounted to 186.62%, i.e. 93.31% of the total amount of spilled fuel oil, while corresponding capacities of the fraction B amounted to 198.45% and 98.72%, respectively (Table 6).

Table 6. Adsorption of engine oil and fuel oil by CELGRAN products

Celgran product	Engine oil (%)	Fuel oil (%)	Fuel oil*
A	102.12 ^f	186.62 ^d	93.31 ^b
B	115.42 ^e	198.45 ^b	98.72 ^a
C	192.47 ^c	213.16 ^a	100.00 ^a
LSD _{0.05}	4.36		1.44
CV (%)	1.43		0.34

*calculated on the basis of the total amount of fuel oil

As the smallest fraction C has the greatest area of granules it is quite understandable that this fraction absorbs the greatest amount of fuel oil. By comparison of obtained results and considering the differences in densities of observed liquids it can be concluded that the CELGRAN products remove more fuel oil than engine oil from water surfaces. These differences are easily observable in fractions A and B that absorbed fuel oil more than engine oil by approximately 84%, and the fraction C by approximately 21%. The CELGRAN products provide the efficient and easy removal of fuel oil from water surfaces as the localisation of a spilled stain is their principal property. A special attention has to be paid to the fuel oil amounts to the CELGRAN product amounts ratio when the fuel oil is removed from water surfaces. In the case of the application of the inadequate ratio and especially when the smallest CELGRAN fraction C is used, certain problems can occur caused first of all by the increase of weight and then by soaking of granules, which will result in less efficient cleaning.

CONCLUSION

The maize cob morphological structure, particularly physical properties and the chemical composition of basic cob fractions provide a wide possibilities for its processing and the production of products indented for different branches of industry and agriculture. However, prior to any processing procedure it is necessary to mechanically pulverise cobs. By grinding, air separation and careful granulation several mill fractions of different granule sizes can be produced. Produced fractions differ from one another in the content of certain groups of compounds, which provides their further refinement into a great number of products. The original technological process of the maize cob processing, by which ligno-celluloses granules of different particle sizes and different physical and chemical compositions are produced, was developed at the Maize Research Institute, Zemun Polje. These granules are used in the chemical industry and the metal processing industry, as well as, in the environmental protection.

Received November 30th, 2004.

Accepted December 27th, 2004.

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GENETIČKA OSNOVA KORIŠĆENJA KUKURUZNOG OKLASAKA KAO VREDNE PRIRODNOOBNOVLJIVE SIROVINE

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Izvod

U Institutu za kukuruz razvijen je originalni tehnološki postupak prerade kukuruznog oklaska kojim se dobijaju lignocelulozni granulati različite veličine čestica. Različit hemijski sastav i fizičko-hemijske karakteristike ovih frakcija, pre svega visoka sposobnost vezivanja tečnosti, naročito ulja i vode opredeljuju njihovu upotrebu kao medijuma za odmašćivanje i sušenje. Velika tvrdoća i abrazivna sposobnost proizvoda dobijenih mlevenjem oklaska našla je primenu za poliranje u metaloprerađivačkoj industriji, a sadržaj nekih jedinjenja (pentozana) od posebnog je značaja u hemijskoj industriji za proizvodnju furfurola i njegovih derivata. Zbog svoje inertnosti, neutralne pH vrednosti i odsustva teških metala ovi proizvodi nalaze primenu kao organski nosači u proizvodnji pesticida i agrohemikalija kao i u kozmetici i farmaciji.

Primljeno 30. XI 2004.
Odobreno 27. XII 2004.