New annual plant (industrial grass) as raw material for pulp and paper industry*

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Summary

Better utilisation of the yearly renewable biomass is an important question in context of the sustainable development. In the Hungarian Great Plain there is plenty of land which is not utilised for food production, so they can be suitable for cultivation of plants for industrial purposes.

Energetic and industrial utilisation of biomass has been investigated for decades worldwide. In Szarvas (Hungary) researchers have selected from Hungarian grasses those which are the most suitable for energetic purposes.

Utilisation of grass ecosystems is very broad scale, the multitude of applications requires careful research and selection of species most suited for a given application. Such research work has great tradition in Hungary. Two of the selected five species are officially approved, three others have been submitted for authorisation.

The recent paper is dealing with the evaluation of different grasses concerning their chemical and morphological composition and the properties of pulps made from such grasses comparing with the traditionally used pulps (wood pulp, straw pulp and pulp from recovered paper).

During systematic investigation the optimal conditions of pulping and bleaching of grasses were determined. It has been concluded that the energy grasses are suitable for the production of both unbleached and bleached pulp. Experimental results show, that about 1/2 of the mass of 1 ton of energy grass can become raw material for paper production, and about 60-65% can be used for the production of heat energy. Fibres obtained from industrial grasses are suitable for the production of packaging and printing-writing papers. Costs of pulp production are about 10% lower when using industrial grass compared to the use of wheat straw.

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Introduction

The words “new raw material” in the title of this presentation refer to a new non-wood perennial plant developed in Hungary under the name „Szarvasi 1 industrial grass”. This grass is the result of decades of plant-breeding work, and it has proven to be a successful renewable energy source. After sowing the grass can be harvested for about 10 years (**Figure 1.**).

Figure 1. Plot of industrial grass

After harvest the second growth can be used for animal feeding until the winter comes. Width of the industrial grass is similar to that of reed, its height can reach 2 meters or even be greater.

Figure 2. Bales of industrial grass

For harvesting and baling of industrial grass machinery of corn cultivation can be used. (**Figure 2.**)

Growing of industrial grass in greater volumes is desirable, because it can serve two important purposes:

1. It is a renewable energy source, which can be produced by the agriculture.
2. It can contribute to the industrial utilisation of several hectares of agricultural land, which can not be cultivated economically any more by the traditional methods.

As the industrial grass contains considerable amount of cellulose it is advisable to utilise it not only for energy production but also in other industrial sectors (e.g. in the paper industry).

Paper has been the carrier of all expressions of human culture until our days. Though its hegemony as information carrier has been limited somehow by the digital data carriers, it remains an important medium in the foreseeable future. As an environment friendly packaging material paper has no real competitor.

Theoretically every source of cellulose is suitable for papermaking. The question whether it can be used for papermaking economically, depends on quantitative and qualitative characteristics of the cellulose content of the given raw material (among them its supermolecular structure), as well as on the composition and ratio of the accompanying materials (incrustation materials). It has been a long-standing effort in the world's paper industry to widen the raw material sources, consisting mainly of wood, with other perennial and annual plants. In Hungary – uniquely in Europe – wheat straw has been used for pulp and paper production for decades, with a technology elaborated in the Paper Research Institute and realised in the Dunaújváros Pulp mill.

The question was, whether the pulp, which can be obtained from the energy grass, is comparable in quality and quantity with the straw pulp produced for papermaking.

Results and discussion

It is known that during the elaboration of the cooking and bleaching technology three important aspects have to be taken into account (among others).

The first aspect is – because of the economic efficiency indices - how much biomass can be produced per hectare. **Figure 3.** shows annual production of biomass in comparison with traditional raw materials.

Type of raw materia	Amount of biomass, suitable for industrial utilisation, t/year
Coniferous trees	1,5 – 2,0
Broad-leaved trees	2,5 – 3,0
Cereal straw	3,5 – 4,0
Flax	2,5 – 3,0
Hemp	6,0 - 8,0
Industrial grass	10,0 – 15,0

Figure 3.: Amount of biomass, which can be produced annually on 1 ha

Based on the table it can be stated that yield of the „Szarvasi-1" industrial grass is 2-5 times more than yield of the conventional papermaking raw materials.

The second aspect is – because of the setting of process parameters – chemical composition of the raw material. **Figure 4**. shows chemical composition of the „Szarvasi-1" industrial grass, in comparison with similar properties of the conventional raw materials.

Chemical composition	Coniferous trees	Broad-leaved trees	Cereal straw	Industrial grass
Extract content (n-hexane)	1,5	1,5	3,5	5,0
Hot water extract	1,0	3,0	16,0	15,0
Holocellulose	65	68	62	67
Lignin content	29	17	13	17
Ash content	1,0	2,0	8,0	3,5

Figure 4. Chemical composition of traditional raw materials and industrial grass samples [%]

Economic efficiency of cooking is determined by the amount of different constituents in the raw material. The amount of lignin determines the energy and chemical requirements, higher ratio of water-soluble constituents reduces the yield and neutralizes part of the cooking chemicals, high content of resins and waxes causes excess consumption of chemicals, high content of minerals (mainly Si-compounds) requires careful control of the chemical recovery process.

The third very important aspect is protection of the environment. For this purpose we have elaborated sulphur-free cooking process and ECF, TCF bleaching technologies in laboratory conditions, using 1kg of raw material per trial.

During experiment planning we changed the temperature, cooking time and amount of chemicals. Based on the results we have defined the optimal cooking technology. Results of morphologic and granulometric tests of pulp produced by the optimal cooking technology are presented in **Figure 5**.

From the comparison of properties it can be seen that pulp made of industrial grass is similar to the pulp made of broad-leaved trees (freeness: 22 °SR, fibre length: 1,16 mm). Due to the higher Kappa number the bleaching process requires more energy (chemicals, temperature, time) to reach the same brightness, but the lower freeness results in better runnability of the pulp on the paper machine.

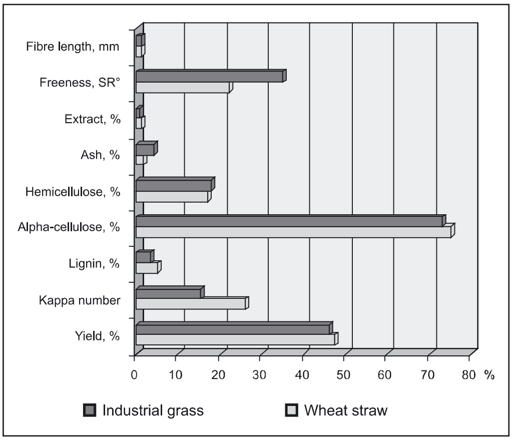


Figure 5.: Relevant properties of pulps produced from industrial grass and wheat straw

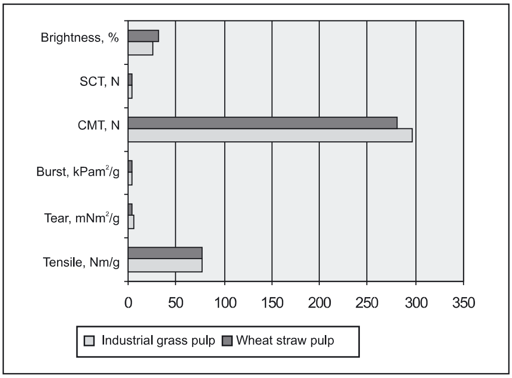
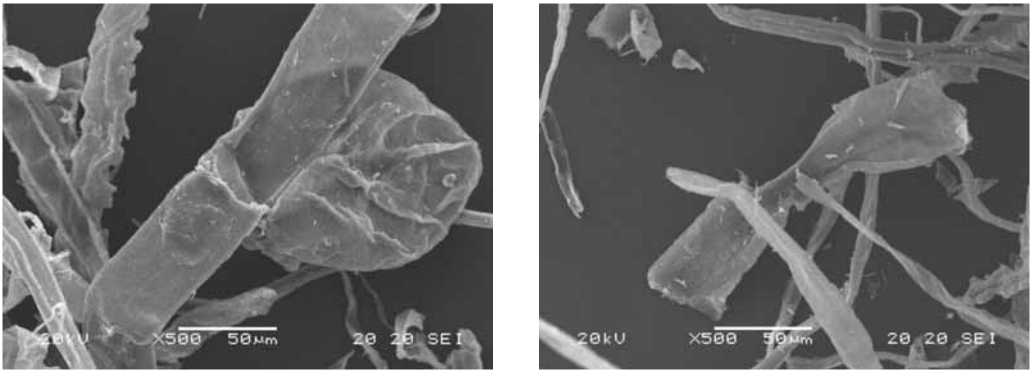


Figure 6. Properties of hand sheets made from unbleached pulps

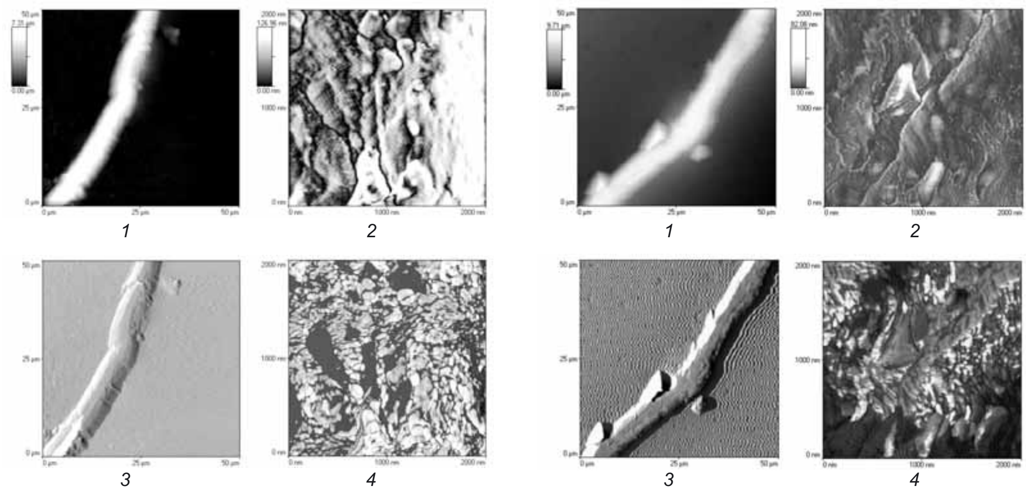
Using the obtained pulps we have produced standard laboratory hand sheets and measured their physical and optical properties. Results of the measurements are shown in **Figure 6**.

When analysing the data it should be taken into account that freeness of the pulp made of industrial grass is only 22 °SR, while that of straw pulp is 35 °SR. Physical properties and brightness are very close to those of paper



Industrial grass *Wheat straw*

Figure 7. Industrial grass pulp and wheat straw pulp, magnification 500x



Industrial grass *Wheat straw*

Figure 8.: Atomic force microscopy photos of industrial grass pulp and straw pulp

made from straw pulp, of course if we increase the freeness of industrial grass pulp, its physical properties will improve and exceed similar properties of straw pulp.

Further on we tested the pulp samples by electron-microscopy (SEM), atomic force microscopy (AFM) and Raman spectroscopy measurements. **Figure 7.** shows electron-microscopy photos of the pulps.

It can be seen from the photos that there are differences between the straw pulp and "Szarvasi-1 industrial grass" pulp, but in both cases majority of the fibres are anisodimensional, and there are several types of isodimensional formations in both pulps.

Diameter of the anisodimensional fibres is characteristic, it was determined from SEM photos of 10^4-magnification. In case of

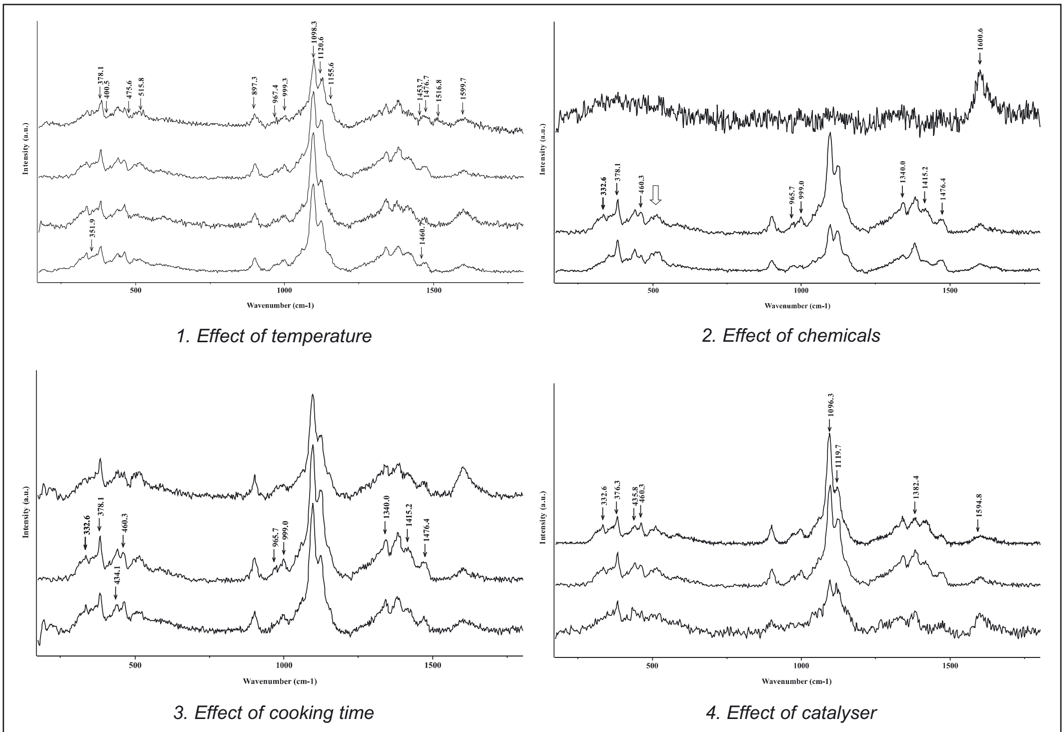


Figure 9. Investigation of the effect of cooking conditions by Raman-spectroscopy (Indrustrial grass)

wheat straw pulp diameter of the fibre is 7,8 μm, in case of industrial grass it is 6,6 μm.

Photos made by atomic force microscopy are shown in **Figure 8**.

In atomic force microscopy scanning is done by a mechanically moved sharp needle. Depending on the regime of measurement topographic and phase pictures can be taken. In the first regime the distance between the sample and the needle is kept constant and the force between the surface and the needle is measured. In the second case the force is kept constant and the distance between the surface and the needle is measured.

From the presented figures the first one is a 50×50 μm topographic picture, number 2. is a 2×2 μm topographic picture, number 3. is a 50×50 μm phase picture, number 4. is a 2×2 μm phase picture. It can be seen from the figures that topographic picture of the pulp made from industrial grass is more serrated, its average roughness is higher. There is only a slight difference between the diameters of wheat straw pulp fibres and industrial grass fibres.

Results of Raman spectroscopic tests are presented in **Figure 9.**

Based on the above curves it can be stated that:

– if we increase the temperature, the lignin content decreases (peak 1098-1120 cm^{-1}), independently of the temperature cellulose I. is in polymorphous state (1),

– if we increase the amount of chemicals, amount of oligosacharides and pectines decreases (peaks 999 and 460 cm^{-1}), degree of hydrolysis and amorphisation increases (increasing ratio of peaks 1120, 1098 cm^{-1}) (2),

N°	SR°	Fibre length mm	κ-number	Lignin %	α-cellulose %	Hemicellulose %	Ash %	Solvent extract,%
0	22	1,16	25,7	4,92	75,15	16,72	1,53	1,10
1	21	1,15	4,6	0,80	78,23	16,87	1,25	0,33
2	18	1,15	5,3	1,10	77,33	16,44	1,32	0,37
3	21	1,11	4,0	0,36	78,89	14,86	1,13	0,43
4	22	1,12	1,9	0,21	83,19	9,78	0,86	0,45
Fsz	42	0,93	0,60	0,13	82,90	9,42	3,60	0,34

Notes: 0 = unbleached, 1 = oxygen, 2 = enzyme, 3 = peracetic acid, 4 = chlorine dioxide, BSP = bleached straw pulp (CEH)
N° = 0-4 = Indrustrial grass

Figure 10. Effect of bleaching stages on chemical and granulometric properties of pulps (N° = 0-4 = Indrustrial grass)

N°	SR°	Tensil length m	Tensile index Nm/g	Elongation %	Tear index mNm²/g	Burst index kPam²/g	Brightness %
0	22	7794	76,46	1,72	5,65	4,17	25,6
1	21	6871	67,60	1,88	6,46	4,26	78,5
2	18	7509	74,04	1,93	7,13	4,93	71,5
3	21	6784	66,74	2,07	6,21	3,96	79,2
4	22	7060	69,45	1,89	5,47	4,37	85,1
FSZ	42	6763	66,16	2,78	5,17	4,34	80,3

Figure 11. Physical and optical properties of bleached pulps

– if we increase cooking time, lignin content decreases (peak 1600 cm^{-1}), degree of hydrolysis slightly changes (3),
– if we increase the amount of catalyser, lignin content decreases (peak 1600 cm^{-1}), amount of the oligosacharides does not decrease significantly (4).

Unbleached pulps produced by the optimal technology have been bleached by ECF and TCF technology. **Figure 10.** shows the effect of bleaching technologies on chemical, morphological and granulometric properties of pulps.

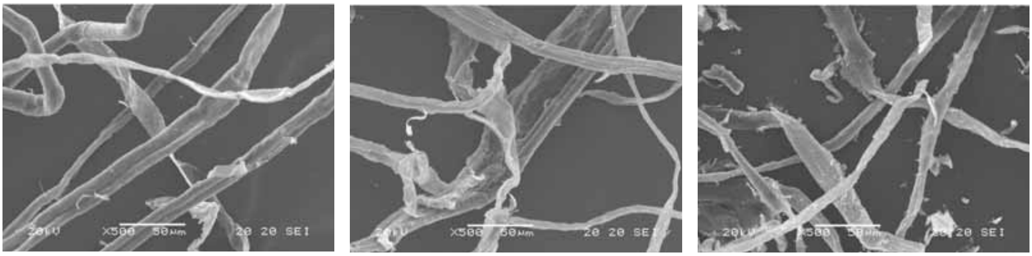
Based on chemical and granulometric properties, it can be stated that freeness of bleached industrial grass pulp is 22 °SR, while that of bleached straw pulp is 42 °SR. Concerning chemical composition, ash content of bleached industrial grass pulp is 1/3 of the ash content of bleached straw pulp.

Unbleached pulp cooked at optimal conditions and various other bleached materials were used for sheet forming. Physical and optical properties of standard hand sheets are presented in **Figure 11**.

Regarding physical and optical properties, freeness differences also have to be taken into account.

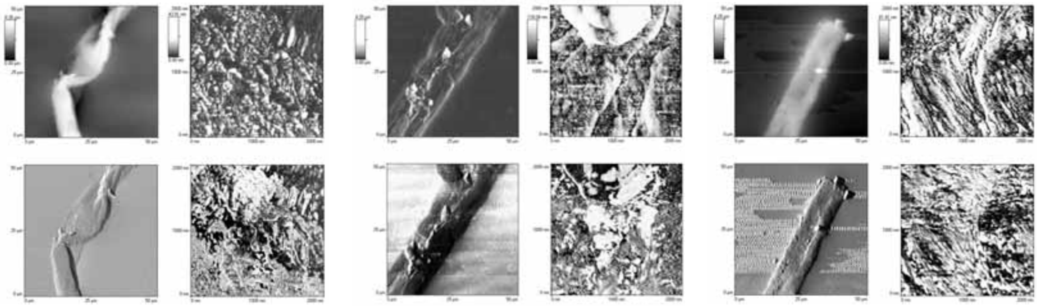
Examining brightness values and comparing them with those of bleached straw pulp, bleaching trials 1. and 3. (TCF) result in similar brightness, while brightness after trial 4. (ECF) is 5 point higher than in case of straw pulp.

Further on we compared the pulp samples by electron-microscopy, atomic force microscopy and Raman spectroscopy tests. **Figure 12.** shows electron-microscopy photos of the pulps.



Bleaching 1 (oxygene) 4,1μm | Bleaching 4. (chlorine dioxide) 5,4 μm | Bleached straw pulp 4,7 μm

Figure 12. Electron-microscopy photos f bleached pulps (500x magnification; 1. and 4. are industrial grass)



Bleaching 1. (oxygene) | Blaching 4. (chlorine dioxide) | Bleached straw pulp

Figure 13. Atomic force microscopy photos of bleached pulps

Based on the photos it can be stated that bleaching results in the reduction of fibre diameter in case of both pulps. There is no big difference between the two pulps, diameter differences are within the margin of error. It can also be stated that parameters of the bleaching technology have smaller effect on the fibre diameter than the cooking parameters.

Atomic force microscopy photos are presented in **Figure 13.**

Based on the photos the following statements can be made:

– During bleaching of wheat straw pulp the residuals of surface dermal tissue are removed, the fibrillar structure can be seen more strongly.

– Heterogenity of the surface can be seen well on the phase photos both in the case of straw pulp and energy grass pulp.

– Surface of the industrial grass fibres changes more during bleaching than surface of straw fibres.

– According to the phase photos, in the course of bleaching the various technologies have stronger effect on surface characteristics of industrial grass fibres than on those of wheat straw fibres.

Results of Raman spectroscopy measurements are shown in **Figure 14.**

It can be seen from the comparison of bleached fibres that structure of the energy grass bands is mostly similar to spectrum of straw fibres.

Ranking of bleaching agents according to their efficiency is the following: 1. chlorine dioxide (bleaching 4), 2. oxygene (bleaching 1), 3. peracetic acid (bleaching 3), 4. enzyme (bleaching 2). Characteristic ratio of bands

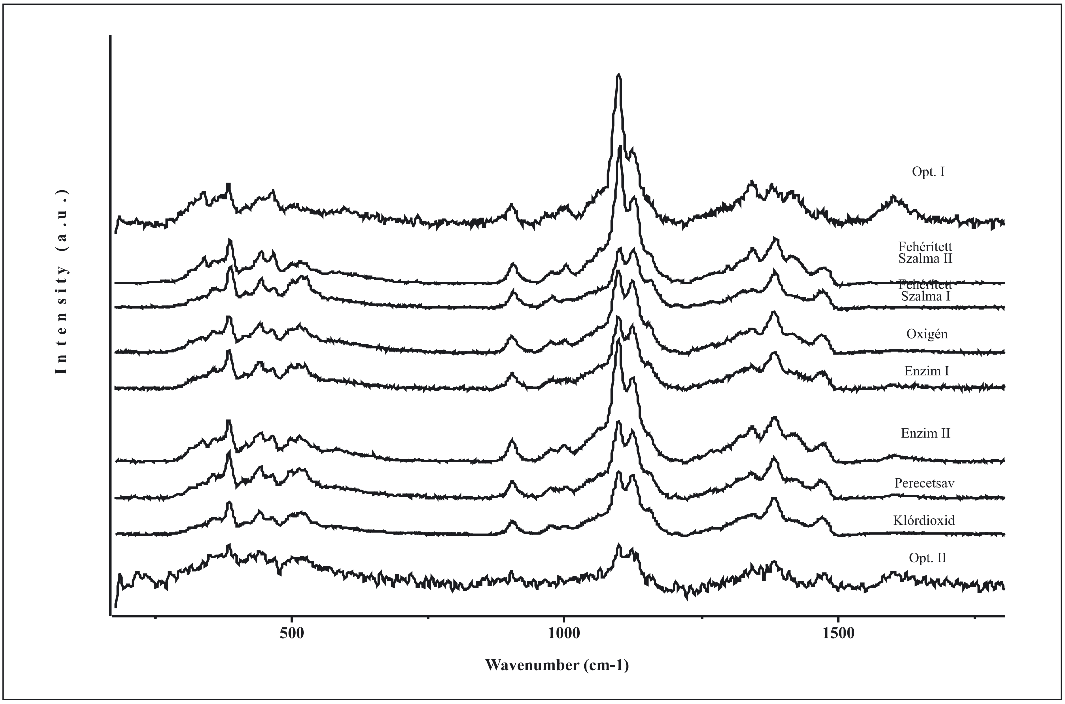


Figure 14. Raman spectroscopy curves of various bleached energy grass pulps

1120 and 1098 cm^{-1} is 1:1, the reason of it is probably the extensive hydrolysis, but there are areas where the 1098 cm^{-1} band is much more intensive (bleached straw II, enzyme II), in these cases the curve corresponds to an undamaged fibre. Such fibres are frequent in straw pulp, but in case of industrial grass the ratio of hydrolysed forms is higher.

Conclusions

- Abundant amount of biomass (annually 10-15 t/hectare) means lower cost of raw material,
- This grass can be cultivated in lower quality soils (e.g. salting soils) which are not suitable for other agricultural purposes,
- Based on morphological and physical tests of unbleached and bleached pulps it can be stated that papermaking pulp produced from „Szarvasi-1 industrial grass” is similar to hardwood pulps from morphological and physical aspects,
- Lower freeness (SR degree) provides better runnability on the paper machine,
- From bleaching processes both the TCF and ECF technologies are suitable for the achievement of good brightness,
- Based on the results of measurements on large-scale instruments it can be stated that Raman-spectroscopy is the most suitable for the follow-up of cooking and bleaching processes. Results obtained by microscopy, SEM and AFM measurements are suitable for the determination of surface and morphological characteristics.

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