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BLACK LOCUST WOOD – PERSPECTIVE RAW MATERIAL FOR PRODUCTION OF CHEMICAL PULP AND GLUCOSE

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Abstract

The potential of Black locust (*Robinia pseudoacacia* L.) wood for production of chemical pulp and glucose was studied. Different clones of Black locust growing in various habitats in Bulgaria were analysed and their chemical composition and density was compared. It was established that the differences in the content of cellulose, lignin, pentosanes and extracted substance in the respective clones were not high and were within the range of 10 % of the corresponding component. Hence, the effect of the chemical composition on the pulp yield was relatively low. The differences in the planting schemes (density) of the Black locust clones had greater influence on the productivity and efficiency of the pulping process. The authors found that *Robinia pseudoacacia* L. has the highest potential in Bulgaria for glucose production. The glucose yield after enzymatic hydrolysis of steam-exploded Black locust is approximately higher in comparison with corresponding treatment of maize stalks, wheat straw and fast-growing poplar and willow. The conclusion is that there are opportunities for plantation harvesting in Bulgaria of separate *Robinia pseudoacacia* L. clones for chemical pulp or glucose for production bioethanol.

Key words: chemical composition, chemical pulp, density, enzymatic hydrolysis, fast-growing trees, *Robinia pseudoacacia* L.

Introduction

The progressive depletion of non-renewable fossil fuels and mankind's growing concern regarding climate change and atmospheric pollution, has led to an interest in the use of renewable fuels. Biomass from plantations of fast growing tree species represents large renewable resources for lignocellulosic bioconversion (González-García et al. 2010). The potential of fast growing forest trees high productivity, coppice ability and ease of vegetative propagation in SRIC plantations has been recognized for over thirty years (Aravanopoulos 2010). The most popular fast growing trees are willow, poplar, eucalyptus, paulownia, etc. The susceptibility of lignocellulosic substrates to cellulose depends on the structural features of the substrate including the cellulose crystallinity, the degree of cellulose polymerization, the surface area, and the lignin content (Ioelovich and Morag 2011). Black locust (*Robinia pseudoacacia* L.) is a fast-growing tree species. It was introduced in Bulgaria more than two hundred years ago (Naydenov et al. 1981). It is considered as naturalized species, which is characterized by high ecological plasticity and is widely spread in the lowlands of the country (Panayotov et al. 2006). It is widely used for wood production, fire wood, as well as for the utilization of degraded and slightly productive lands and soil erosion control. In addition, Black locust is used for feeding of bees and highly valued honey is produced. The timber texture is considered by many people as equally beautiful as that of mahogany and teak, while the strength characteristics are often higher than those of oak and beech wood. Black locust wood has wide application in the woodworking industry and for production of bleached cellulose (Panayotov et al. 2005). In Bulgaria the share of the species is about 2.5 % of the total forest area and the interest to this tree species constantly increases. During the period 2005–2010, its area has increased with 7.13 % from 139,855 ha to 150,590 ha. For the same five-year period the stock wood has increased with 984,832 m^3. During the last twenty years the attention of the scientific community was directed towards improvement and establishment of more productive clones with improved production qualities (Tsanov et al. 1990). More than 100 sample trees were planted, a method for vegetative planting by root seedlings was developed, clonal seed orchards were established. During the last 20 years the company Lignum Bulgaria – Ruse established more than 12,000 dka of crops for the production of large-sized timber with vegetative seedlings of selected clones by using scientific consultations and clones from the Experimental Station for Fast-Growing Tree Species in Svishtov (Kalmukov 2002, 2005, 2007). Yet, the high clone variety is still not well studied. This is needed to provide possibilities for a more differentiated usage of the important clones.

The aim of this paper is to study the timber of selected Black locust clones and to evaluate this raw material for production of chemical pulp and glucose as sources for bioethanol production of second generation.

Material and Methods

Characteristics of the conditions for plant growth of the sample trees

The samples for analysing the physical and chemical properties wood from the separate Black locust clones are taken from the clone collection in the village of Vardim (43°36′33.3″ N, 25°29′22.8″ E), district of Veliko Tarnovo, Northern Bulgaria. The nursery at the Experimental station at Vardim village is situated on the second terrace of the Danube river. The soil is calcic chernozems, according to the new classification-brown (WRBSR 2006). The parent material is sandstone. The terrain is flat. The ground water level is above 8 meters. The carbonates in the surface horizon are above 3.5 %. The soil reaction in a water extract is alkaline, from 7.63 to 7.95. According to the mechanical properties of the soil, it can be classified as heavily sandy-clayey. The water-and-physical properties are good. The porosity is 50 %. The capacity of active soil moisture in one meter soil layer is 217 mm and in the two-meter layer it is 452 mm. For the last 25 years the average annual quantity of rainfall is 510.9 mm with precipitation sum of 236.6 mm April-August.

The Black locust clones collection is created in 1995 and 1996 and more than 50 clones are used. Before the plantation, full soil preparation was carried out. One-year-old seedlings produced by root seedlings were used for planting. The forestation is carried out in 30/30/30 cm handmade holes. The initial planting scheme is 3.0×3.0 m. In the first three years the seedlings are entrenched 3 times and the space between the rows is disc-plowed 3 times during the growing period. In the following years one disc-plowing between the rows is carried out.

Characteristics of the Black locust trees

For analysis, washers from breast height (1.30 m) from the sample trees were taken. The clone ′Jazskiseri′ is considered the best in Hungary. It is distinguished by faster growing and straight trunk. The crown takes ½ of the height. It is used for the production of technological chips, semi-mechanical pulp, fibreboards and particleboards. In Bulgaria it is one of the clones with good growth. The self-pruning of the trunk was 11 m. The height of the tree was 17.95 m and diameter at breast height was 22.2 cm. The tree was 19-year-old. The clone has been researched at a young age – 8 years under the code B54 within the project "Danube-Agro".

The clone ′Pordim′ is selected in the region of the Game Hunting Station Pleven (Fig. 1). The terrain was flat with slightly frayed black soil (Highlight). The clone was distinguished by good growth and straight trunk. The self-pruning of the trunk was 8.3 m, the height was 18.20 m, the diameter 24.8 cm. The tree was 18-years-old. The clone has been studied at a young age – 8 years under the code

Clone ′Jazskiseri′ **Clone ′Pordim′** **Clone ′Tsarevets′**

Fig. 1. Plantations of Black locust clones.

B4 within the project "Danube-Agro". This previous study pointed out the clone to be with the hardest wood.

The clone 'Tsarevets' is selected from the region of the State Game Station Svishtov (Fig 1). The crop is announced to be for seed base. The terrain is steep with a southern exposure. The soil is calcic chernozem. This clone is distinguished with good growth and productivity and withstands soils with the availability of carbons in the surface horizon. The tree was 18 years old with diameter of 23.4 cm. The trunk was self-pruned to the height of 10 m. The height of the tree was 18.30 m. So far this clone has not been included into previous studies.

All clones were promulgated vegetative through root cuts and the mother trees were kept.

Chemical analyses

Chemical analysis of the raw materials is based on the following methods: cellulose (Kurschner and Hoffer 1993), lignin (TAPPI standard T222 om-11), pentosans (BDS 11449:1973), ash (TAPPI standard T211 om-12) and substances soluble in hot water (TAPPI standard T207 cm-08). The craft cooking is carried out with hand cut and sorted chips with average length of 20 mm thickness 4–6 mm. The chips (100 g oven dried) are cooked in 2 dm^3 stainless steel laboratory autoclaves rotated at a constant rate in a polyglycol bath. The liquor-to-wood ratio during cooking was 4:1. The sulfidity was 12 % and the active alkali charge is varied from 17 to 20 % as Na_2O.

The cooking is started at 80 °C and the durations of the heating time to the full cooking temperature 165 °C was 140 min, while the H-factor varied from 1000 to 1500. The black liquor impregnation and pre-steaming was carried out at 100 °C for 30 min at atmospheric pressure before cooking and the total black liquor charge was the same as in the conventional cooking regime. The Kappa number is measured according to ISO standard (ISO 302:2004).

The steam explosion pre-treatment of wood chips is performed in 2 dm^3 stainless steel laboratory installation at the following conditions: liquid to solid ratio was 10:1; initial temperature was 100 °C; maximum temperature was 200 °C; pressure was 15.85 bar; heating time was 60 min followed by additional 10 min at the maximum temperature. The steam exploded lignocelluloses was washed with distilled water and subjected to enzymatic hydrolysis.

Enzymatic hydrolysis

The cellulose complex NS22086 with activity 1000 BHU/g and β-glucosidase NS22118 with activity 250 CBU/g of Novozymes AS were used for the enzymatic hydrolysis. The enzyme charge of NS 22086 was 5 %, while that of NS 22118 was 0.5 %, both referred to dry mass of the lignocellulose. The enzymatic treatment is carried out in polyethylene bags in a water bath previously heated to 50 °C; pH was 5.0–5.6 and reaction time was 48 h. The glucose content is analysed with a Dionex HPLC system, according to the NREL standard laboratory analytical procedure.

Results and Discussion

Different clones of Black locust growing in various habitats in Bulgaria have been investigated and comparison has been made of their chemical composition and

Table 1. Chemical composition and density of wood from different Black locust.

Tree species	Lignin, %	Cellulose, %	Pentosans, %	Ash, %	Substances soluble in hot water, %	Oven dry wood density, kg/m³
Black locust 'Pordim'	27.5	48.7	21.3	0.32	6.6	769
Black locust 'Tsarevets'	23.0	49.0	22.9	0.43	3.7	659
Black locust 'Jazskiser'	27.7	45.4	21.0	0.61	7.9	734
Black locust without bark from different clones	21.1–27.5	44.4–49.1	17.5–22.9	0.2–0.7	3.7–9.8	600–855
Black locust with bark from different clones	21.2–28.6	43.9–49.1	-	1.7–2.8	-	-
Common beech	24.2	45	24.2	0.7	2.6	680

density (Table 1). It has been established that the difference in the content of cellulose in the respective clones is 10 %, while difference in the content of lignin, pentosans and extracted substances were within the range of 25 % of the corresponding component. Highest cellulose content and lower amount of lignin was established in Black locust 'Tsarevets' having the lowest density. The determined up to 25 % differences in the wood density of the Black locust clones can exert comparatively greater influence on the productivity and effectiveness of the cellulose production processes.

Svilocell EAD plant use mixed hardwood species such as Turkey oak, Sessile oak, Black locust, Common beech and Common hornbeam (Table 2).

Poplar is used as an individual brand. It is known that the properties of pulp from Black locust are similar than these obtained from mixed hardwood without Black locust. But, a problem is found during the blowing of Svilocell pulp.

The effect of cooking conditions on the Kappa number and pulp yield of Black locust with different density is investigated (Tables 3 and 4).

It has been established that to achieve a Kappa number below 20 after cooking of Black locust clone 'Tsarevets' with the lowest density (659 kg/m^3), the alkali charge should be 18.5 % Na_2O at H-factor

Table 2. Hardwood species used in Svilocell.

Hardwood species	Amount, %
Common beech	11.5
Turkey oak	50.5
Sessile oak	5.6
Common hornbeam	15.9
Black locust	16.5

Table 3. Cooking parameters for the Black locust 'Tsarevets' with low density.

A.A. charge as Na_2O, %	Sulfidity, %	H-factor	Kappa, number	Screening yield, %	Total yield, %
17 % Na_2O	12	1000	25.0	-	-
17 % Na_2O	12	1200	23.4	-	-
18.5 % Na_2O + Steaming	12	1200	21.4	36.5	-
18.5 % Na_2O	12	1500	22.0	38.8	-
18.5 % Na_2O + Steaming	12	1500	19.8	43.9	45.7

1500. On the other hand, due to the higher density, the Black locust clone 'Pordim' is cooking more difficult and needs a higher alkali charge of 20 % to achieve Kappa number 23.8; moreover the total yield and screening yield was lower.

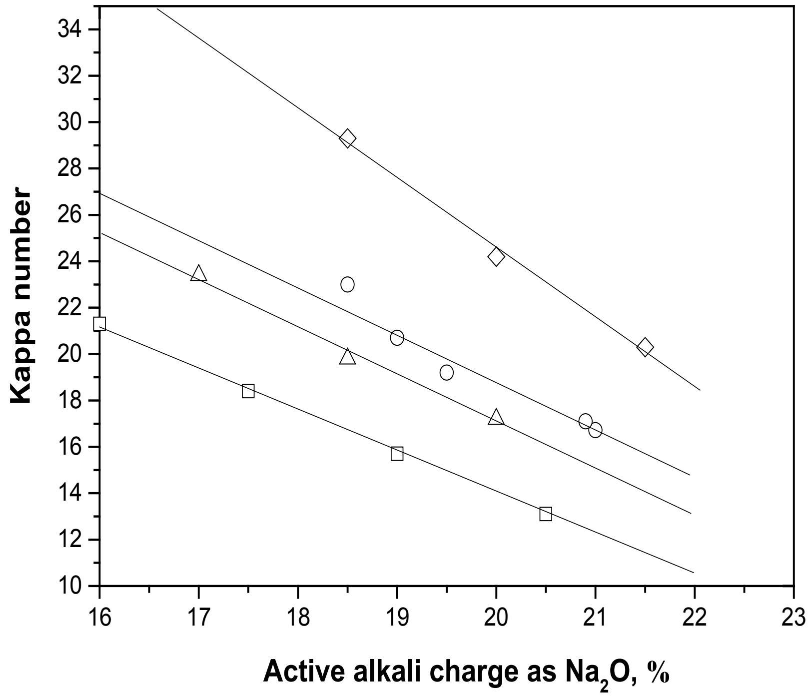
Figure 2 shows that Black locust clone 'Tsarevets' with the lowest density is cooking easier than Svilocell's mix wood (Table 2), but more difficult in comparison with the common beech.

As it can be seen from Figure 3, the dependence between total pulp yield and Kappa number for low density Black locust clone 'Tsarevets' and common beech was on the one line, while this dependence for high density (769 kg/m^3) Black locust clone 'Pordim' and Svilocell's mix is on the another line.

The potential of Black locust wood as a source for glucose production was also researched. Steam explosion pre-treatment

Table 4. Cooking parameters for the Black locust 'Pordim' with high density.

A.A. charge as Na_2O, %	Sulfidity, %	H-factor	Kappa, number	Screening yield, %	Total yield, %
17 % Na_2O	12	1200	33.3		-
18.5 % Na_2O	12	1200	31.0		-
18.5 % Na_2O	12	1500	29.3	32.4	-
20.0 % Na_2O	12	1500	27.8	38.5	-
20.0 % Na_2O + Steaming	12	1500	23.8	40.9	43.2



Legend: □ – Common beech; Δ – clone ′Tsarevets′; ○ – Svilocell's mix; ◊ – clone ′Pordim′.

Fig. 2. Effect of the active alkali charge on the pulp Kappa number after cooking of different wood.

of the wood samples before enzymatic hydrolysis was carried out. During the pretreatment, process to 32–38 % of the wood were dissolved, especially due to removal of hemicelluloses (Table 5).

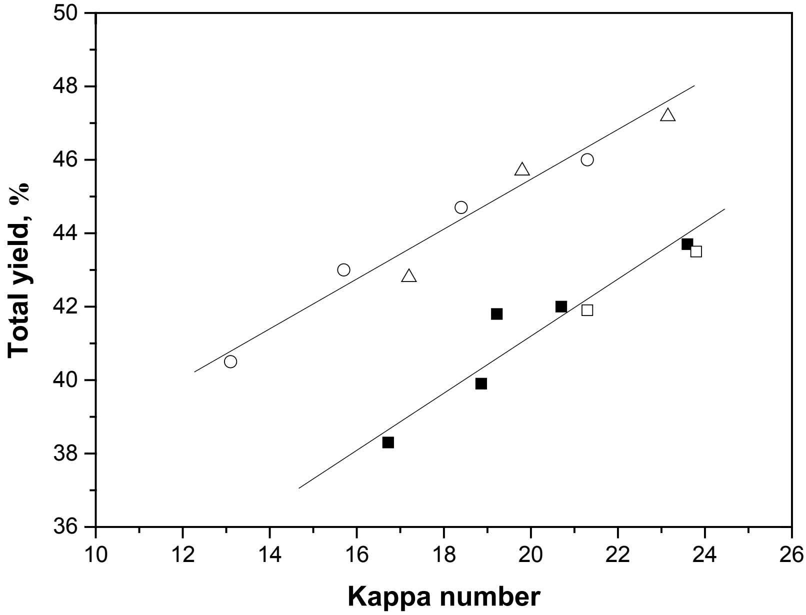
The results of enzymatic hydrolysis of pre-treated samples of Black locust with different density is presented on Figure 4. The best result was obtained for low density Black locust ′Tsarevets′, while the glucose yield for high density wood of Black locust ′Pordim′ was 25 % lower.

Table 5. Chemical composition of pulp after steam explosion.

Tree species	Lignin, %	Celluloese, %	Ash, %	Yield, %
Black locust ′Pordim′	30.4	70.0	0.5	64.41
Black locust ′Tsarevets′	29.1	72.8	0.4	66.98
Black locust ′Jazskiser′	37.6	63.3	0.6	66.80

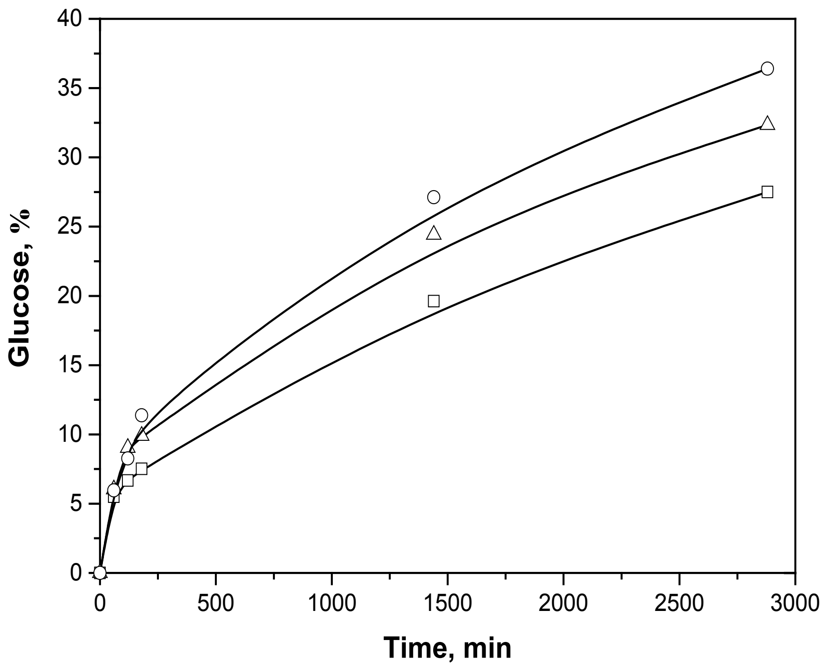
The dependence between wood density and glucose yield after enzymatic hydrolysis is presented on Figure 5.

Comparison of various wood species showed that enzymatic digestibility of pretreated samples of *Paulownia tomentosa* (Thunb.) Steud., *Robinia pseudoacacia*



Legend: ■ – Svilocell's mix; □ –clone ′Pordim′; Δ – clone ′Tsarevets′; ○ – Common beech.

Fig. 3. Dependencies between total yield and kappa number after cooking of different wood species.



Legend: ○ – clone ′Tsarevets′; Δ – clone ′Jazskiseri′; □ – clone ′Pordim′.

Fig. 4. Glucose yield after enzymatic hydrolysis of pre-treated different clones of Black locust.

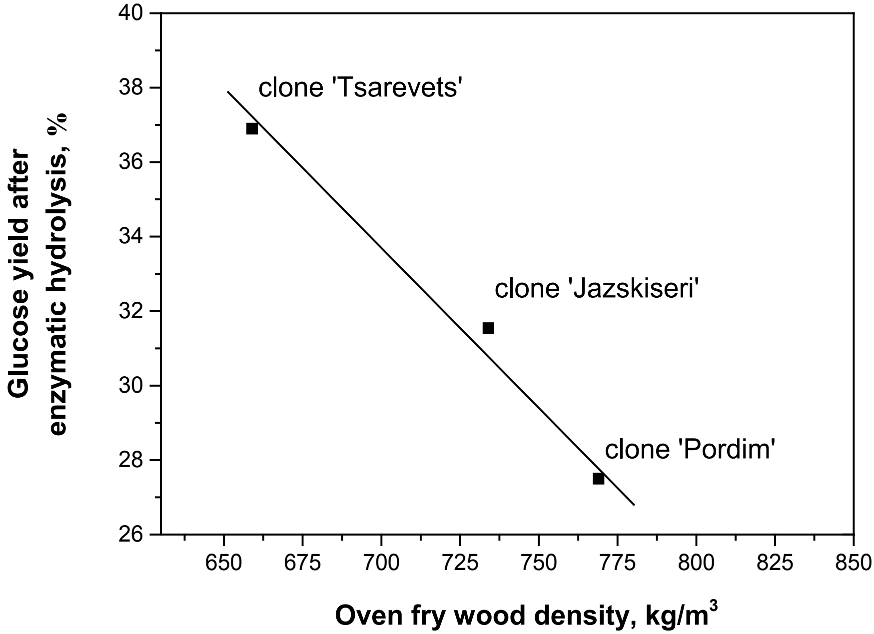


Fig. 5. Dependence between wood density and glucose yield.

Legend: 1 – Populus alba; 2 – Robinia pseudoacacia; 3 – Paulownia tomentosa; 4 – Paulownia elongata.

Fig. 6. Glucose yield after enzymatic hydrolysis of pre-treated samples.

and especially of *Paulownia elongata* S.Y.Hu, was higher than that of *Populus alba* L. (Fig. 6).

Conclusions

A correlation is established between chemical composition and density of wood for Black locust different clones. The highest cellulose content and the lowest amount of lignin was observed for low density wood of Black locust ′Tsarevets′.

The wood of Black locust ′Tsarevets′ with the lowest density can be used for production of kraft pulp. On the other hand, to obtain delignified kraft pulp from high density Black locust ′Pordim′, the cooking conditions must be very strong.

The low density Black locust ′Tsarevets′ has a great potential for conversion in glucose to produce second-generation bioethanol. It is found that the glucose yield after enzymatic hydrolysis of steam-exploded Black locust was higher in comparison with other typical fast-growing tree species of Bulgaria. A correlation between the yield of glucose and wood density is found.

There are possibilities the plantation harvesting in Bulgaria of separate Black locust clones having low density wood, which can be used for production of chemical pulp and glucose.

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