SWEET SORGHUM BIOMASS QUANTITATIVE AND QUALITATIVE CHARACTERISTIC DEPENDING ON HYBRID AND TYPE OF SOIL
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КІЛЬКІСНА ТА ЯКІСНА ХАРАКТЕРИСТИКА БІОМАСИ ЦУКРОВОГО СОРГО ЗАЛЕЖНО ВІД ГІБРИДІВ ТА ТИПУ ҐРУНТУ

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ABSTRACT
Ukrainian and American sweet sorghum hybrids were studied as raw material under reclaimed lands conditions in the southeast Ukraine. Among the cultivars in the range of hemicellulose destruction the highest reactivity was recorded for American hybrids, whereas the process of cellulose decomposition was most active in Ukrainian hybrids. Thermogravimetry (TG) curves of Ukrainian hybrids were more differed for plants grown on loess like loam comparative with American hybrids. The molecular structure of sweet sorghum lignin is represented by the spatially hindered hydroxyl groups of alcohol and phenolic type with the strength hydrogen bonding between some other structural fragments of macromolecules, ordinary carbon-oxygen bonds of metoxyl groups, and double carbon-carbon bonds.

РЕЗЮМЕ
Українські та американські гібриди цукрового сорго вивчалися як сировина в умовах рекультивованих земель південного Сходу України. Стадія випаровування води і видалення летких компонентів у біомасі американських гібридів проходила в інтервалі більш високих температур. Криві ТГ українських гібридів різнились більше у рослинах, що були вирощені на лесоподібному суглинку, порівняно з американськими гібридами. Молекулярна структура лігніну цукрового сорго представлена просторово ускладненими гідроксильними групами спиртового і фенольного типу з міцним водневим зв'язком між деякими іншими структурними фрагментами макромолекул, звичайними вуглець - кисневими зв'язками метоксильних груп і подвійними вуглець - вуглецевими зв'язками

INTRODUCTION

It is known that sorghum has highly efficient C4 photosynthesis, high water use efficiency, and high tolerance to drought, salt, high or low temperature, and poor or low soil fertility (*Taylor et al., 2010; Wang et al., 2012*). Large - scale planting on marginal lands would require improved varieties with optimized biofuel-related traits and tolerance to biotic and abiotic stresses (*Mathur et al., 2017*). In fact, sweet sorghum ability to adapt to marginal growing conditions is main pre-requisite to provide significant amounts of feed stuff and energy (*Cavalaris et al., 2017*). A novel approach for the bio-refining of sweet sorghum stem is application where biodegradable material is required (*Yu et al., 2012*). In the recent years, sweet sorghum residues have been considered as lignocellulosic material that could serve as feedstock for second generation biofuels (*Anfinrud et al., 2013; Kumar et al., 2008; Zolotovs'ka et al., 2016*). Currently in Ukraine there are more than 1.1 million hectares of degraded, unproductive and technologically polluted lands (*Fileccia et al., 2014*). Among the sources of destructive environmental impact, one of the first places is occupied by mining enterprises. In the process of their production activity, the natural initial relief is disturbed, and lands on which mineral resources are directly mined, as well as areas for storing waste rocks, are withdrawn from agricultural use.

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During open-cast mining, rocks of past geological epochs are carried onto the earth's surface, and, when interacting with the atmosphere, are exposed to intensive weathering (*Sheoran et al., 2010; Menendez and Loredo, 2018*). Substrates formed in this way significantly differ from zonal soils by the level of fertility, physical, physicochemical, agrochemical and other ecologically important characteristics. Even after prolonged reclamation, such lands are unproductive and may contain phytotoxic compounds (*Boruvka et al., 2005; Navarro et al., 2008*). Sweet sorghum is genetically diverse and variations exist for characteristics such as juice sucrose concentration, total stalk sugar yield, fresh stalk yield, biomass yield and others indicating potential for improvement (*Regassa et al., 2014*). It was possible to provide a selection process to obtain sweet sorghum hybrids with high cellulose and hemicellulose content (*Zhao et al., 2009*).

The main objective was to give sweet sorghum biomass quantitative and qualitative characteristic depending on sweet sorghum hybrid and type of soil.

MATERIALS AND METHODS

Field experiments were carried out for two years (2017 and 2018) in Dnipropetrovsk province situated in the south-eastern part of steppe zone of Ukraine and particularly in the Pokrov land reclamation station of Dnipro State Agrarian and Economic University. In recent years, there has been a gradual increase in the average monthly air temperature with a simultaneous decrease in the amount of precipitation during the vegetation period. Eight sweet sorghum hybrids of Ukrainian and American selection *(Medove, Zubr, Pokrovske, Silosne-42, SS506, Sioux, Mohawk, G1990)* were investigated in the field experiments. Experiments were carried out in two versions. In the first case the plants were grown on long-term plant meliorated loess-like loam (LLL), in the second - on the black soil (BS) mass taken in stockpiling. The pH was 7.4 -7.6. The humus content in the loess-like loam is about 1.1%, while in the black soil it is 3.3. The experimental design was a randomized complete block with 3 replications. Sorghum seeds were sown in early May.

Sweet sorghum lignin structure was studied with methods of IR absorption spectroscopy. The IR absorption spectra of lignin were recorded with a SPECTRUM ONE (PerkinElmer) instrument. The samples for recording were prepared using the standard procedure with KBr (*Smith et al.,1987*). The quantum-chemical calculations have been carried out with the help of Gaussian 03, Revision E.01 package of programs (*Frisch et al., 200*4) at the *DFT*-PBE1PBE/6-311++G(d,p) level of theory. The spectral characteristics of located stationary points have been achieved by using the harmonic vibrational frequency approximation. The thermal analysis of plant biomass was carried out using the derivatograph Q-1500D of the "F. Paulik-J. Paulik-L. Erdey" system. Differential mass loss and heating effects were recorded (*Carrier et al., 2011; Wróblewski and Ceran, 2016*). The results of the measurements were processed with the software package supplied with the device. Samples of biomass were analyzed dynamically at a heating rate of 10°C/min in an air atmosphere. The mass of samples was 100 mg. The reference substance was aluminum oxide. All the results obtained were treated by statistical methods using the StatGraphics Plus5 software package at significance level of 0.95 % (P-value < 0.05).

RESULTS

It was revealed that thermolysis of biomass passed in the temperature range from 20-50°C to 530-590°C and consisted of two periods. The first period was represented by one stage, at which the water evaporation and the active removal of volatile components took place. This process was accompanied by an expressive endothermic effect. Depending upon the sorghum cultivar and type of substrate, the temperature interval of this stage was within 20°C-150°C for Ukrainian hybrids, and within 40°C-190°C for American hybrids (Table 1 and fig.1).

The analysis of the rate of change in mass showed a single peak in this region. In samples grown on the black soil, the mass loss varied within 6.1-10.1%. In samples grown on loess-like loam, the mass loss was lower, in the range of 3.2-7.5%, with the exception of Silosne - 42 (20.4%). The rate of destruction at this stage was small and did not exceed 15%/min. However, in the samples of the Silosne - 42 taken on loess-like loam, the rate of decomposition was significantly higher (23.2%/min), indicating a high content of volatile components in biomass of plants growing on this substrate.

The second period embraced three stages which were represented by the thermal reactions sum of decomposition of individual constituents: hemicellulose, cellulose and lignin.

At the same time, the intervals of these components destruction partially overlapped. The temperature of 150°C-160°C was the beginning of the exothermic reactions passing.

The main process of hemicellulose and cellulose decomposition passed in the temperature interval 180°C-734,00°F, implied two stages and was characterized by one or two peaks in this range (Fig.2). In this temperature range, a small fraction of the lignin also decomposed, but without expressed peaks. The stage of hemicellulose and cellulose destruction was accompanied by the greatest mass loss (55-67%).

Table 1

Data of Ukrainian and American hybrids of sweet sorghum biomass thermal degradation.

Type	Temperature interval [°C](temperature of maximum rate of decomposition [°C]) Mass loss [%]				The share of residual mass [%]
Zubr					
S	40–140 (100) 6.8	140–220 (190) 17.0	220–390 (280) 40.6	390–570 (430) 30.4	5.2
LL	30–120 (90) 3.2	120–250 (220) 35.2	250–380 (270) 31.8	380–530 (410) 19.8	10.0
Medove					
S	40–140 (110) 8.6	140–220 (190) 13.6	220–380 (270) 47.4	380–550 (430) 24.0	6.4
LL	30–130 (90) 6.4	130–210 (180) 14.2	210–390 (270) 50.2	390–540 (440) 20.4	8.8
Pokrovske					
S	50–130 (110) 6.4	130–200 (150) 9.2	200–350 (270) 47.6	350–570 (390) 27.2	9.6
LL	30–130 (90) 4.4	130–230 (200) 17.6	230–360 (270) 44.0	360–550 (430) 26.8	7.2
Silosne - 42					
S	20–130 (100) 7.0	130–220 (190) 15.6	220–380 (270) 46.6	380–560 (430) 24.4	6.4
LL	30–140 (80) 20.4	140–230 (190) 25.2	230–330 (270) 31.8	330–420 (340) 12.6	10.0
Mohawk					
S	50–180 (110) 6.87	180–300 (290) 24.24	300–390 (320) 33.73	390–590 (460) 28.89	6.27
LL	50–160 (110) 6.87	160–400 (280) 58.98		400–560 (420) 25.25	8.9
SS506					
S	50–160 (100) 7.4	160–390 (290) 58.2		390–560 (430) 24.8	9.6
LL	50–180 (100) 7.47	180–300 (280) 31.11	300–390 (310) 27.27	390–550 (450) 26.87	7.28
G1990					
S	40–190 (100) 10.1	190–380 (310) 54.94		380–550 (440) 25.86	9.1
LL	40–180 (100) 7.19	180–300 (280) 28.97	300–390 (310) 26.86	390–570 (540) 25.46	11.52
Sioux					
S	40–180 (100) 6.08	180–390 (280) 55.52		390–570 (410) 23.6	14.8
LL	50–180 (90) 7.2	180–290 (280) 22.2	290–380 (310) 33.6	380–550 (440) 25.4	11.6

Among the cultivars in the range of hemicellulose destruction the highest reactivity was recorded for American hybrids, whereas the process of cellulose decomposition was most active in Ukrainian hybrids.

During the last stage of thermolysis (360°C-590°C) thermal decomposition of cellulose and lignin is completed, the carbonated residue combusts as well. At this stage, the most pronounced exothermic effect emerged.

The weight loss was 23.6-30.4% (black soil) and 12.6-26.9% (loess-like loam). TG curves of Ukrainian hybrids were more differed for plants grown in loess like loam comparative with American hybrids.

The rate of decomposition was small for all cultivars and substrates and varied from 6.2 %/min to 11.4 %/min. G1990, Zubr and Pokrovske had higher reactivity than others hybrids. The most complete combustion of biomass (except for the Pokrovske, SS506 and Sioux) was observed on black soil.
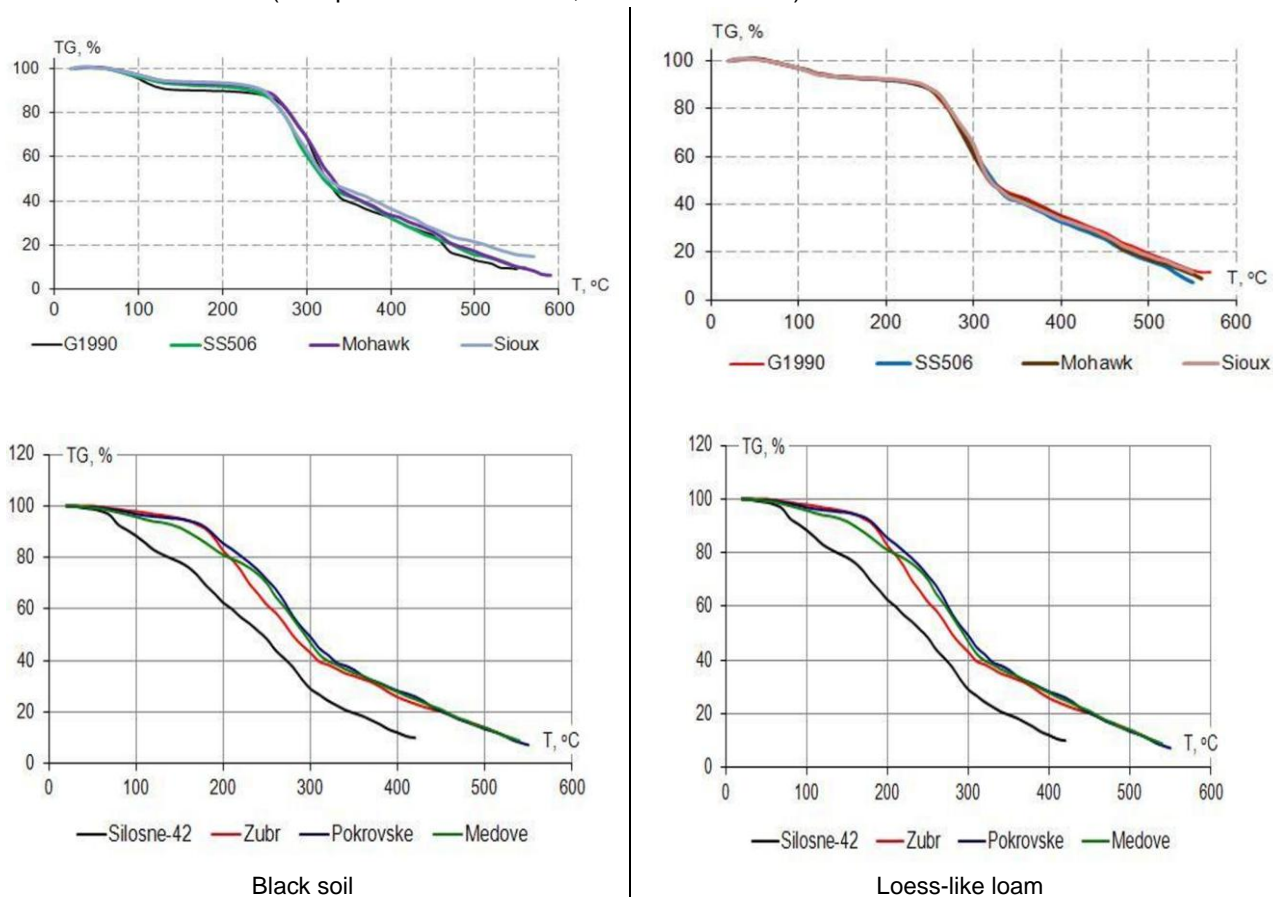

| | |
| Black soil | Loess-like loam |

Fig. 1 - TG curves of sorghum biomass thermal destruction

The activation energy of thermal-oxidative degradation is a universal sensitive criterion for assessing the thermal stability of biomass. Based on the calculation of the kinetic parameters of different stages of biomass thermal decomposition, it was found that the thermal stability of various sorghum samples is somewhat different. The values of the activation energy of the American and Ukrainian hybrids did not differ significantly and were in the range of 55.0-66.2 kJ mol^{-1} on black soil at the stage of volatile components removal. At the stage of hemicellulose and cellulose decomposition, the activation energy indices in American hybrids practically did not change, while in Ukrainian hybrids they decreased almost twice and varied within 28.5-31.9 kJ mol^{-1} (Table 2). Thus, for the destruction of molecular bonds at this stage, it is required to apply a greater amount of energy to the biomass of American hybrids than for the Ukrainian ones, which indicates a higher rate of thermal stability of their biomass. It is revealed that the type of substrate can affect the thermal stability of biomass. In American hybrids G1990 and Mohawk, a decrease in activation energy (by 5.5-10.9%) was observed at both stages of biomass decomposition, and vice versa, in hybrids SS506 and Sioux, this indicator increased by 5.6-11.4%. In all Ukrainian hybrids, at the first stage, a medium (12.2-19.5%) and significant (32.1 - 42.5%) decrease in the activation energy value was noted. At the second stage, the activation energy of the hybrids Pokrovske and Zubr was higher than at the first stage by 10.4% and 22.3%, respectively, and lower by 3% and 27.8% in the hybrids Medove and Silosne-42.

It is known that sorghum feedstock has a high volatile content while a low fixed carbon ratio that indicates a lower lignin composition in the biomass (*Dhyani et al., 2017*). According to data in sweet sorghum bagasse average content of cellulose, hemicelluloses and lignin are 34-45%, 15-25%, and 12-18% respectively (*Bakeer et al., 2013*). Lignin is known to impede conversion of plant biomass to pulp or biofuels.
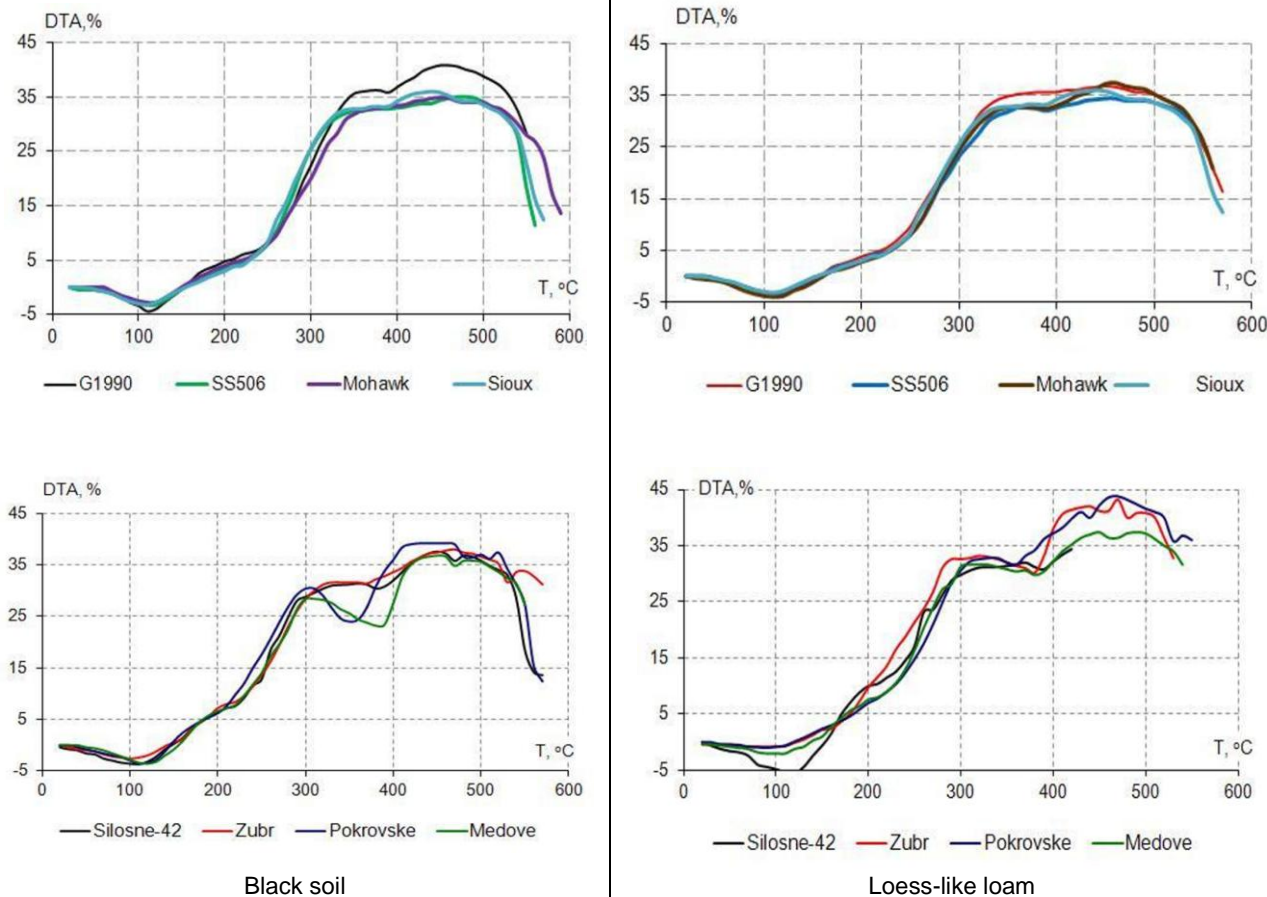
Black soil   Loess-like loam

Fig. 2 - DTA curves of sorghum biomass thermal destruction

Table 2

The kinetic characteristics of sorghum biomass thermal - oxidative degradation

Sorghum hybrid	Stage of biomass decomp osition	Black soil		Loess-like loam	
		Approximation dependence, (correlation coefficient R)	Activation energy [kJ mol^{-1}]	Approximation dependence, (correlation coefficient R)	Activation energy [kJ mol^{-1}]
Mohawk	I*	-2.6375x + 4.0095 (R=0.99)	65.84	-2.446x + 3.7291 (R=0.98)	60.22
	II	-0.7663x - 0.9664 (R= 0.91)	63.60	-0.8727x - 0.646 (R=0.95)	60.07
SS506	I*	-2.4769x + 3.8082 (R=0.99)	55.03	-2.5468x + 3.9102(R=0.97)	61.30
	II	-0.7575x - 0.8531 (R= 0.94)	57.52	-0.8181x - 0.741 (R= 0.96)	57.87
G1990	I*	-2.5954x + 4.0259 (R =0.98)	63.93	-2.3516x + 3.5436 (R=0.99)	59.58
	II	0.4706x - 1.2099 (R=0.87)	66.24	-0.8659x - 0.6674 (R=0.98)	59.04
Sioux	I*	-2.1499x + 3.2183 (R=0.99)	64.41	-2.2165x + 3.3902 R=0.99)	67.37
	II	-0.5949x - 1.4405 (R² = 0.93)	63.36	-0.681x - 1.0866 (R=0.97)	59.78
Zubr	I*	-2.4123x + 3.8734 (R=0.98)	60.25	-2.0001x + 3.2684 (R=0.99)	48.47
	II	-1.7493x + 1.5718 (R=0.94)	28.25	-2.7913x + 3.6333 (R =0.99)	34.53
Medove	I*	-2.2985x + 3.7155 (R=0.98)	56.45	-2.1829x + 3.5084 (R=0.98)	38.35
	I	-2.6237x + 3.9057 (R=0.96)	29.75	-2.4449x + 3.4016 (R=0.96)	28.89
Pokrovske	I*	-2.1553x + 3.418 (R= 0.99)	66.18	-2.3482x + 3.744 (R=0.98)	38.02
	II	-3.343x + 5.5522 (R=0.99)	31.86	-1.5993x + 0.8747 (R=0.97)	35.16
Silosne-42	I*	-2.4598x + 3.9316 (R=0.98)	61.18	-2.1706x + 3.9713 (R=0.99)	53.69
	II	-1.8765x + 1.9653 (R=0.95)	29.85	-1.8565x + 3.0096 (R=0.98)	21.52

I - stage of volatile components removal, II - stage of hemicellulose and cellulose decomposition

The removal of lignin from plant biomass is a costly process; hence, research efforts are now aimed at designing genotypes that either deposit less lignin or produce lignin that are more amenable to chemical degradation (*Sticklen, 2006*). Lignins are characterized by the extreme complexity of the chemical structure, heterogeneity in the monomeric composition and types of intermonomeric links.

Unlike cellulose, which has the same structure for all plants, there are no identical lignins in nature (*Davin and Lewis, 2005; Vanholme et al., 2010*). The main building blocks of lignin are the hydroxycinnamyl alcohols (or monolignols) coniferyl alcohol and sinapyl alcohol, with typically minor amounts of p-coumaryl alcohol (*Rippert et al., 2009*). To study the sweet sorghum lignin macromolecules by method of IR absorption spectroscopy, some model structures have been chosen as the typical building blocks such as p-coumaryl (A), coniferyl (B) and sinapyl (C) alcohols with trans-configuration of double carbon-carbon bond in these molecules. Some final geometries have been located at DFT-PBE1PBE/6-311++G (d,p) level of theory. The relatively uniform nature of the overestimation of quantum-chemical harmonic vibrational frequencies for a particular theoretical procedure allows the application of generic frequency scale factors, which in the case of PBE approximation are 0.9904 and 0.9944 for basis sets 6-31+G(d,p) and 6-311+G (d,p), respectively (*Merrick et al., 2007*). The results of calculations as well as some experimental parameters of IR absorption spectra are in Table 3 and Figure 3.

Table 3

Some harmonic vibrational frequencies [cm⁻¹], obtained experimentally as well as calculated at PBE1PBE/6-311++G(d,p) level of theory

Intensity, band shape[1]	Theoretical model			Experiment	Interpretation
	A	B	C		
v. s., wd.	3879	3878	3877	3417–3438	$v_{(OH)}$ of alcohol groups, capacity of moisture
	3871	3801	3793		$v_{(OH)}$ of phenolic groups, capacity of moisture
av.	–	3084	3087	2917–2938	$v_{(CH3)}$ of methoxyl groups
		3016	3017		
w.	3016	3015	3016	2833–2854	$v_{(CH2)}$ of hydroxymethyl groups
	2971	2970	2970		
w.	1729	1728	1729	1719–1729	$v_{(CC)}$ of carbon-carbon double bonds
av.	1674	1671	1661	1615–1625	$v_{(CC)}$ of benzene rings
	1552	1559	1555	1480–1510	
w.	–	1499	1497	1408–1427	$\delta_{(CH3)}$ of methoxyl groups
		1461	1453	1365–1378	
w.	1384	1329	1363	1245–1250	$\delta_{(CC)}$ with $\delta_{(CH)}$ of benzene rings
v. s.	1063	1064	1064	1041–1052	$v_{(CO)}$ of methoxyl with hydroxymethyl groups

Symbols explanation: s. – strong, av. – average intensity, w. – weak, wd. – wide, v. – very; v – stretching vibrations, δ – bending vibrations.
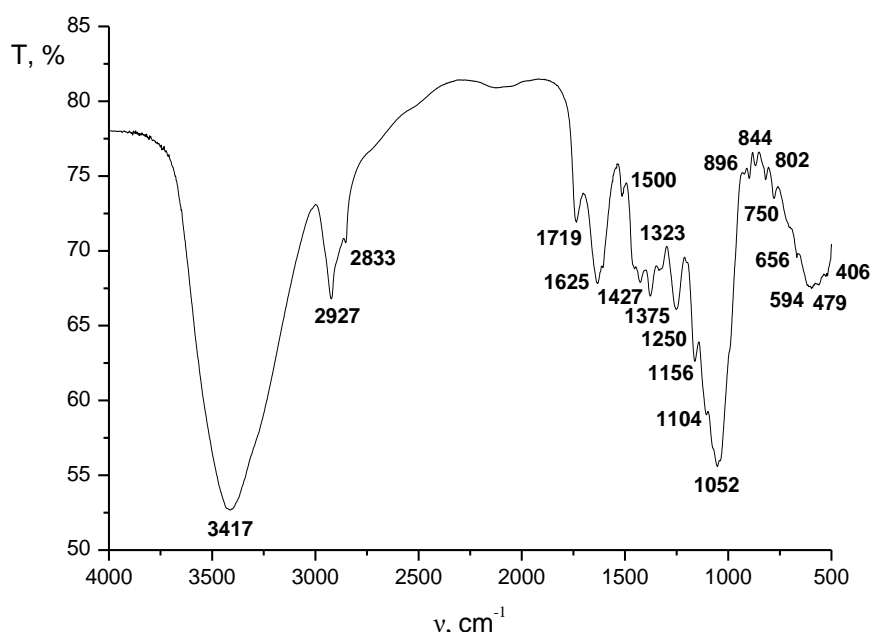

Fig. 3 - The typical IR absorption spectrum of native lignin material derived from saccharine sorghum

Analysis of the results showed that the most intensive absorption bends are in area 3417–3438 and 1041–1052 cm^{-1}. For the first one, mainly deals with the stretching vibrations of spatially hindered hydroxyl groups of alcohol or phenolic type with the strength hydrogen bonding between some other structural fragments of macromolecules.

For the second one, some intensive stretching vibrations of ordinary carbon-oxygen bond of metoxyl groups have the main contribution with predominance of intra-molecular hydrogen bonding effects, which occur at the distances about 2.050–2.070 Å. There are also two typical stretching vibrations of benzene rings at 1625 and 1500 cm^{-1}. As to the area 1719–1729 cm^{-1}, there is only one not very intensive fringe giving by the stretching vibrations of double carbon-carbon bonds. However, this band may be interpreted as a conjugated carbonyl group's signal. In fact, such type structural fragments usually have much more intensive bands with shifting in area ~1750 cm^{-1}. Finally, some average sets of theoretical versa experimental wave numbers, which are shown below correlate to each other:

$$v,\delta(\text{expt.}) = (124.82\pm54.09) + (0.89\pm0.02) * v,\delta \text{ (theor.)};$$
$$r=0.997; \; s_0=74.58; \; n=13.$$

The proposed theoretical models are validated in reflection of spectral and energetic parameters for investigating systems.

ACKNOWLEDGEMENT

CONCLUSIONS

Thermolysis of dry sorghum biomass took place in the temperature range from 20-50°C to 530-590°C. The stage of water evaporation and removal of volatile components passed in the interval of higher temperatures in the biomass of American hybrids. Among the cultivars in the range of hemicellulose destruction the highest reactivity was recorded for American hybrids, whereas the process of cellulose decomposition was most active in Ukrainian hybrids. TG curves of Ukrainian hybrids were more differed for plants grown on loess like loam comparative with American hybrids. It is required to apply a greater amount of energy for the destruction of molecular bonds at stage of main components degradation to the biomass of American hybrids than for the Ukrainian ones, which indicates a higher thermal stability of their biomass. The most complete combustion of biomass (except for the Pokrovske, SS506 and Sioux) was observed on black soil. The molecular structure of sweet sorghum lignin is represented by the spatially hindered hydroxyl groups of alcohol and phenolic type with the strength hydrogen bonding between some other structural fragments of macromolecules, ordinary carbon-oxygen bonds of metoxyl groups, and double carbon-carbon bonds.

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