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Resource-Efficient Methods for Obtaining Fibre Semi-Finished Products and Their Practical Application

I. V. Trembus, N. V. Mykhailenko, and A. S. Hondovska

National Technical University of Ukraine
'Igor Sikorsky Kyiv Polytechnic Institute',
37, Beresteiskyi Ave.,
UA-03056 Kyiv, Ukraine

Prospects for non-wood plant raw materials' usage and environmentally friendly methods of obtaining fibrous semi-finished products in comparison with those, which are most widely used today, are analysed. As determined, the usage of agricultural waste and annual plants as raw materials for obtaining cellulose is quite promising today. Main advantages and disadvantages of using such raw materials for industrial needs are formulated. The study shows that non-wood plant materials have chemical composition similar to wood plant material. It is carried out analysis of processing some agricultural waste such as sunflower stalks, wheat straw, miscanthus, *etc.*, using ethanol, hydrogen peroxide, glacial acetic acid as reagent. It is determined the influence of technological parameters such as process temperature and duration on physical and mechanical parameters of paper. Research results show that increasing process duration reduces cellulose yield and content of residual lignin, and in most cases, improves physical and mechanical parameters. As established, for semi-finished products' production of appropriate quality with optimal properties, it is necessary to select technological parameters separately for each type plant raw material. First of all, this is caused by different morphological structure and chemical composition of raw materials. Fibrous semi-finished products obtained from non-wood plant raw materials by organosolvent methods are characterized by quite good physical and mechanical parameters. Some ways of using cellulose from non-wood plant raw materials for production of paper, cardboard, microcrystalline cellulose, nanocellulose and filtration membranes are highlighted. As established, such products can already be used both in various industries and for household purposes.

Проаналізовано перспективи використання недеревної рослинної сировини й екологічно більш чистих методів одержання волокнистих напівфабрикатів у порівнянні з тими, що найбільш масово використовуються у промисловості сьогодні. Показано, що використання відходів сільського господарства й однорічних рослин в якості сировини для одержання волокнистих напівфабрикатів є перспективним. Сформульовано основні переваги та недоліки використання такої сировини для промислового застосування. Показано, що недеревна рослинна сировина має хемічний склад, подібний до листяних порід деревини. Проведено аналізу можливости одержання волокнистих напівфабрикатів з деяких відходів сільського господарства, таких як стебла соняшнику, пшеничної соломи, міскантусу та ін. з використанням етанолу, пероксиду водню, льодяної оцтової кислоти в якості реаґенту. Визначено вплив технологічних параметрів, таких як температура та тривалість варіння на фізико-механічні показники готової продукції. Результати досліджень показали, що збільшення тривалости варіння зменшує вихід целюлози та вміст залишкового лігніну й у більшості випадків поліпшує фізико-механічні показники. Встановлено, що для виробництва напівфабрикатів належної якости з оптимальними властивостями потрібно підбирати технологічні параметри окремо для кожного виду рослинної сировини. Це зумовлено, в першу чергу, різною морфологічною будовою та хемічним складом сировини. Волокнисті напівфабрикати, одержані з недеревної рослинної сировини органосольвентними способами, характеризуються достатньо гарними фізико-механічними показниками. Висвітлено деякі шляхи використання целюлози із недеревної рослинної сировини для виробництва паперу та картону, мікрокристалічної целюлози, наноцелюлози та фільтраційних мембран. Встановлено, що така продукція вже сьогодні може використовуватися як в різних галузях промисловости, так і в побутових цілях.

Key words: non-wood plant raw materials, agricultural waste, organosolvent cooking, fibrous semi-finished products, delignification, physical and mechanical parameters, paper, cardboard, nanocellulose, filtration membrane.

Ключові слова: недеревна рослинна сировина, відходи сільського господарства, органосольвентні варіння, волокнисті напівфабрикати, делігніфікація, фізико-механічні показники, папір, картон, наноцелюлоза, фільтраційна мембрана.

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1. INTRODUCTION

Development and application alternative methods for cellulose production are very important tasks today. Usage of energy-efficient, ecological and resource-saving methods is urgent task in development new technologies for pulp production. For this purpose, it is necessary to use widespread and fast growing raw materials as well as methods and technologies of its processing that exclude usage of toxic substances or those that have difficulties in regeneration.

Thus, selection of annual plants and agricultural waste as raw materials in combination with organosolv delignification methods allows approaching creation resource-efficient technologies for pulp production.

Sulphite and sulphate delignification methods of plant raw materials are the most widely implemented for pulp production nowadays. On the one hand, they are characterized by high process efficiency and economy and make possible to produce pulp with various quality indicators. On the other hand, these methods are quite environmentally unfriendly and characterized by large amount water and air pollution during technological processes [1, 2].

Usage of oxidative-organosolvent methods can be alternative options for pulp production. Such methods are characterized by usage of cheaper chemical reagents such as monoatomic and polyatomic alcohols, carboxylic acids, ketones, ethers, esters, phenols etc. Molecular oxygen, hydrogen peroxide or nitric acid various concentrations are used as oxidants. Titanium oxide, sodium molybdate, sodium tungstate, citric acid and others are used as delignification process catalysts. Organosolvent technologies allow processing at lower temperatures and atmospheric pressure if compare with sulphite and sulphate methods. Another, but not less important advantage of such methods is fact that organic solvents have selective effect on lignin. This property makes possible to produce pulp with higher polysaccharides yield and use simpler chemical regeneration schemes in production, which also has less environmental impact [3–7].

Thus, pulp industry in recent years has demonstrated promising production increasing in the world with value of approximately 180 million tons per year, and this figure is constantly growing. Wood is used as main raw material for pulp production in the world. However, such raw materials are characterized by low reproducibility and constantly decreasing reserves. For example, technological maturity of birch (*Betula pendula*), aspen (*Populus tremula*) and hornbeam (*Carpinus bentulus*) plantations is reached after 40–50 years from the moment of planting, pine (*Pinus sylvestris*) or fir (*Picea abies*)—after 70–90 years, and oak (*Quercus robur*) or beech (*Fagus sylvatica*)—after 100–120 years [8–10].

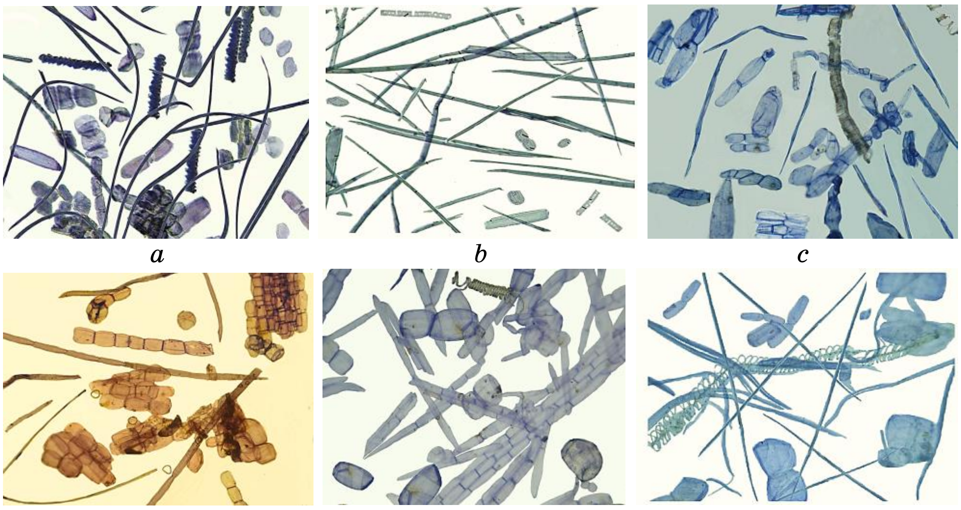
2. THEORETICAL PART

Bulk density, boiler loading density and moisture content are important physical characteristics of plant materials that have huge impact on pulp processing as well as paper production. These physical characteristics are general quality indicators of raw materials and show it profitability for pulp processing and sustainable for production cardboard and paper products, cellulose membranes and pulp for chemical processing. Bulk density determines transportation costs, pulp production capacity, chemicals and energy consumption. The loading density shows amount of plant material in absolutely dry state that can be fed into reactor. Density of raw material is also one of the most important characteristics that affect to production high-quality pulp, cardboard and paper products. In addition, it has huge impact on strength indicators and various other pulp physical properties. Thus, density of raw material and pulp yield can be used to estimate amount of plant material required for production of one ton of air-dry pulp. Physical properties of plant raw materials and agricultural waste are quite different. They depend on species, place of cultivation, plant age, *etc.* [2, 11].

Non-wood plant raw materials can be used as promising alternative to generally accepted materials for pulp production. Compared to wood, non-wood plant materials have similar cellulose content, lower lignin content, higher hemicellulose and silicate content. Advantages of non-wood plant material include that it is mostly byproduct of agriculture, is cheaper than wood, has large volumes of production in relatively short time and requires little cleaning before usage. Unfortunately, this raw material has its own disadvantages that limit the scope of its usage. It can be called low bulk density, relatively short fibres, high silicic acids and small inclusions contents. Accordingly, there are such side problems of its usage as unprofitable transportation and storage, very fast rotting, which causes high losses. However, it should be noted that potential availability and cost-effectiveness of using agricultural waste and other annual and perennial plants are quite attractive, despite existing limitations [12].

All types of non-wood plant material can be conditionally divided into two groups, which are based on their anatomical, morphological structure and chemical composition. First group includes different types of raw materials with high cellulose content 75–85% and low lignin content 1–2%. This raw material has strong and long fibres with size more than 10 mm. This group includes cotton fibres, cotton lint, bast fibres of flax and hemp. This raw material allows obtain fibrous semi-finished products for chemical processing, high-quality paper, special valuable types of paper.

The second group include predominant part of non-woody plants with cellulose content of 31–59%, lignin of 10–25% and pentosanes of 18–27%. The fibres are characterized by shorter size than plants' fibres in first group of raw materials and reach length of 0.3–2.0 mm. This group includes straw fibres of grain and technical crops, oil crops stalks, sugar cane bagasse, common and dry cane, bamboo, kenaf, miscanthus, *etc.*



a *b* *c* *d* *e* *f*

Fig. 1. Microscopic structure of stalks: (*a*)—wheat; (*b*)—rape; (*c*)—sunflower; (*d*)—corn; (*e*)—sylphium sylph; (*f*)—amaranth (magnification 8·10).

It is important to have raw materials with sufficient α-cellulose content and low pentosanes content during processing non-wood plant raw materials to obtain high-quality pulp. The fibres structure should facilitate easy access of chemicals to cellulose molecules, non-cellulosic impurities should be easily removed and content of parenchymal cells should be low. Microscopic structure of agricultural waste stems and some types of non-wood plant material are shown in Fig. 1, *a*–*f*.

Special feature of cereal crops stems is fact that they have covering layer (epidermis) saw-like shape. Ring and spiral cells are less common. The main part of industrial crops stems is long, narrow, and thick-walled with pointed ends (sclerenchyma fibres). In addition, they have vessels with bordered pores and vessels with spiral thickening, which destroy in pulp processing. Large percentage parenchymal cells are made up. They are characterized by diversity in both shape and size: from short, barrel-shaped to elongated. Transitional forms are also often found [13, 14].

Different morphological parts of non-wood plant raw materials are not equivalent for pulp and paper industry according to their chemical composition (Table). For example, in agricultural waste, stalks are the most valuable and suitable for technological needs [13]. They have the highest cellulose and the lowest mineral contents. Other morphological parts are less valuable like leaves, inflorescences, spikelets, and also they can be harmful due to high ash content. First of all, it is silicon oxide, which leads to great technological complications during pulp production and reduces quality of product [15–17].

Large pentosanes number in non-wood plant raw material stems

TABLE. Chemical composition of annual plants and agricultural waste.

Raw material	Cellulose	Lignin	Solubility		Resins, fats wax	Pento-sanes	Achiness
			H_2O	NaOH			
Spruce (*Picea abies*)	46.1	28.5	7.3	18.3	2.93	10.7	0.18
Birch (*Betula pendula*)	41.0	21.0	2.2	11.2	1.8	28.0	0.47
Amaranth (*Amaranthus candatus*)	31.9	26.5	17.9	35.6	0.4	19.8	3.4
Cotton (*Gossypium hirsutum*):	38.7	22.5	7.5	18.3	3.9	19.2	4.6
fibre	62.9	11.8	2.1	15.9	4.2	23.5	4.5
stem	36.3	25.9	8.8	26.2	3.0	18.2	4.8
Rye (*Secale cereale*) straw:	45.2	19.3	9.9	36.9	5.8	26.2	4.6
stem	55.8	19.8	7.9	34.9	4.6	25.6	3.6
leaf	41.7	17.4	10.8	36.5	7.2	26.3	7.3
ear	38.9	14.0	16.3	38.2	5.1	28.0	7.1
Kenaf (*Hibiscus cannabinus*)	52.4	15.9	8.9	26.1	2.21	25.5	3.3
Cannabis (*Cannabis savita*):							
bast	46.2	17.0	6.9	25.0	1.2	20.2	2.6
wooden	67.8	6.5	3.8	20.8	1.9	15.6	1.5
part	42.2	12.5	5.1	22.9	3.7	21.7	2.9
Corn (*Zea mays*)	42.6	17.9	10.1	18.7	3.0	25.7	3.9
Linen (*Linum usitatissimum*):	59.6	10.9	4.1	13.6	4.7	16.8	2.4
fibre	69.5	6.1	3.7	13.4	3.6	5.1	1.5
chaff	42.0	23.6	5.2	19.4	5.2	25.1	2.8

Continuation of TABLE.

Raw material	Cellulose	Lignin	Solubility		Resins, fats wax	Pento-sanes	Achiness
			H_2O	NaOH			
Miscanthus (*Miscanthus giganteus*)	42.9	24.4	6.1	24.4	4.8	23.4	2.7
Sunflower (*Helianthus annuus*)	40.6	20.1	5.6	35.2	—	21.3	3.0
Soy (*Glycine max*)	41.8	19.7	11.3	23.8	2.9	24.6	2.5
Sverbig (*Bunias orientalis*)	34.3	22.0	25.4	35.7	1.4	19.9	9.8
Wheat (*Triticum L.*)							
straw:	44.3	16.5	10.1	38.4	5.2	26.7	6.6
stem	46.2	18.6	6.0	36.2	4.6	26.4	4.2
leaf	42.3	15.2	9.8	40.1	6.5	27.4	9.4
ear	39.0	17.6	12.0	42.2	7.0	31.2	8.6
Rapak (*Brassica napus L.*):							
stem	35.6	22.9	11.6	25.6	4.8	27.6	6.9
root	28.3	27.7	10.9	31.5	2.4	25.1	5.4
pods	22.6	12.8	18.3	29.2	4.0	23.8	4.0
Cane (*Phragmites australis*)	41.8	21.0	7.2	18.3	1.2	22.7	4.4
Sorrel (*Rumex patientia L.*)	37.8	21.4	1.4	26.0	1.4	21.9	5.1

make possible to claim that pulp, which are made from them, have good papermaking properties. In addition, they are suitable for cellulosic base manufacturing for filter-membranes' production [18, 19]. Cellulose content is the main factor that determines possibility of using plant raw materials for pulp production. In agricultural waste stamps and non-wood plant raw materials, it ranges from 32 to 60%; so, it can be argued that they are suitable for pulp production [20, 21].

3. RESULTS AND DISCUSSION

Research in field of fundamentally new waste-free technologies for cellulose obtaining is conducted in variety directions. These researches include cellulose biological synthesis, enzymatic delignification of plant materials and solvolytic delignification in organic solvents [18–21].

Hydrogen–alcohol method of cellulose obtaining was one of the first among organosolv methods for cellulose obtaining thankfully to series of Kleinert's patents [22]. He proposed carry out wood delignification using 50% water solution of ethanol or methanol. Hydrogen–alcohol digestion of cellulose began at pH close to neutral and ended at pH = 2.8–3.8. Boiling was carried out in countercurrent continuous reactor at temperature 195°C.

The main disadvantages of this delignification method are that, under such conditions, only dark fibrous mass with low viscosity can be obtained and process is carried out at high temperatures. Authors of research [23] implemented previous experience of hydrogen-alcohol brews in process called ALCELL. It is based on boiling cellulose with 50% water solution of ethanol at temperature 195°C, pressure 2.8 MPa, and duration 60 minutes. Obtained pulp was bleached according to *D–L–D* scheme. Whiteness index of ALCELL cellulose reached 90%. The obtained organosolv wood pulp was used for coated papers production. Proposed method is accompanied by high-pressure usage, which makes it unsuitable for industrial realization.

Authors of research [24] proposed to use sunflower stalks as raw material for pulp production. In this way, hydrothermal treatment of plant raw materials was carried out using 70% ethanol as cooking solution in a ratio of 8:1 to solid raw materials, at temperature 170°C for 120 minutes. Cellulose with quality indicators approaching sulphate cellulose was obtained as a result of delignification process. The product has such characteristics: yield of solid residue of 36.3%, cellulose content of 69.1%, hemicellulose of 12.7%, residual lignin of 8.2%. In addition, the physical and mechanical quality indicators of cellulose samples obtained by boiling with using ethanol were not inferior to sulphated cellulose [24].

There is well-known ecological method of obtaining pulp from miscanthus stems in laboratory conditions. It is includes pretreatment with water–alcohol solution of sodium sulphite and sodium hydroxide in volume ratio of 80:20. Anthraquinone was used as delignification catalyst, temperature of process varied from 130 to 170°C, and pretreatment time was varied from 90 to 180 minutes. It should be noted that compliance with such conditions for organosolv process are determined as optimal for many representatives of non-wood plant materials [25].

Further processing of hydrolysed raw materials includes heat treatment with solution containing acetic acid and hydrogen peroxide in ratio 1:1 with addition sodium tungstate as catalyst. Treatment temperature was of 105°C and duration of 180 minutes. It was established that increasing delignification temperature in process of miscanthus stems in range from 130 to 150°C leads to pulp yield reduction and content of residual lignin also contributes to increase physical and mechanical indicators. Further increase of process temperature to 170°C and duration to 120 minutes leads to decreasing physical and mechanical parameters of obtained product. It can be assumed that this is the reason of destruction carbohydrate part partial in plant material under such conditions. It should be noted that cellulose from miscanthus obtained using organosolv method have high quality indicators and, as author noted, can be used for production various types paper and cardboard [25, 26].

The authors of work [27] proposed ecological method of obtaining cellulose. It is characterized by hydrothermal treatment of annual plants and agricultural waste such as wheat straw, rapeseed, amaranth, sverbiga, oxalate, with solution that consists of hydrogen peroxide and glacial acetic acid. Processing was carried out at temperature of 95°C and duration from 60 to 180 minutes. As a result, it can be noted that increasing duration of delignification process more than 90 minutes leads to decreasing cellulose yield and content of residual lignin for all representatives of non-wood plant material. This regularity is connected with fact that during increasing duration of lignin and polysaccharides oxidation greater percentage of low molecular weight, mineral and extractive substances passes into solution. In addition, it should be noted that cellulose obtained in such way from all studied plants is characterized by relatively high degree of whiteness. Peracetic acid has ability not only to oxidize lignin but also to decolorize its chromophoric groups [27].

Having analysed results of research [27], it is worth noting that differences in indicators of completeness, physical and mechanical indicators of cellulose in delignification process are connected with various factors. The main and most influential should be called anatomical structure of plant raw materials. First of all, it affects on depth and speed processes of reagents penetration into intercellular space of raw materials as well as different chemical composition, which will directly affect on lignin reactivity. In addition, results of research indicate that oxidation of lignin and its transition into cooking solution for specified plants occur with different intensity that can be explained both by different lignin content in plant raw material and by its different structure. Cellulose yield and residual lignin content will decrease in case of increasing delignification process duration. This is can be easily explained by greater influence of reaction mixture on components of plant raw material. Physical-mechanical indicators for most obtained pulp from non-wood plant raw materials also increase with increasing duration. However, process duration will negatively affect on quality indicators in product as for oxalate. First of all, it is depend on chemical composition. This is explained by the fact that in this case processes of destruction will prevail over processes of delignification. This leads to decreasing in functional structural units that give strength to finished product [27].

Alternative delignification method of vegetable raw materials includes thermal pretreatment with formic acid and hydrogen peroxide solutions [7]. During conducting experiment with different reagents ratio $HCOOH:H_2O_2$, it was determined that increasing in content of formic acid leads to decreasing in cellulose yield. This may be related to intensification process of lignin splitting which is consequence of breaking α- and β-alkyl-aryl ether bonds in lignin macromolecule, dissolution extractive substances, mineral substances and carbohydrates of plant raw materials and their transfer into the cooking solution. It should be noted that excessive increase in content of formic acid increases straw cellulose yield due to partial lignin condensation in acidic environment. Thus, there is increasing amount of residual lignin at formic acid content more than 50%. This dependence is explained by lignin partial condensation reactions, which are activated during decreasing pH of cooking solution [7].

Promising directions in development technologies for organosolvent processing using vegetable raw materials are also related to usage of various catalysts in delignification process. Their presence allows increase cellulose content in final product.

Peroxocomplexes of transition elements such as sodium tungstate or sodium molybdate are used as catalytic additives. The catalytic delignification scheme includes interaction H_2O_2 with Na_2WO_4 and formation peroxocomplex Na_2WO_8. Such complex contributes to oxidation process of acetic acid to peroxoacetic acid with simultaneous regeneration Na_2WO_4 [28–29].

Decreasing in residual lignin in cellulose was observed for ratio of ethanol to additive from 1:0.1 to 1:0.02 during addition nonylphenol, resorcinol or pyrocatechin in amount 1–5% of weight absolute dry raw materials [33].

Group of scientists [30–32] conducted study based on catalysis wood delignification with hydrogen peroxide–acetic acid–water with sodium tungstate, molybdate (Na_2WO_4 and Na_2MoO_4) and phosphorotungstic acid ($H_3PW_{12}O_{40}$) as catalyst [30]. Usage of these catalysts during treatment wood in solution $AcOH:H_2O_2:H_2O$ in ratio

50:15:35 makes possible to deepen significantly delignification process. Research was conducted at temperature of 80°C, duration of 60 minutes and a hydromodule 10:1. Sawdust chips were used as raw material. Results of these research showed that cellulose yield did not decrease as in case of used sulphuric acid. Na_2WO_4 and Na_2MoO_4 showed the highest selectivity in delignification process [31].

Authors in work [3] propose to use citric acid as catalyst in cellulose obtaining process in order to reduce general cost, which is less expensive, if compare with molybdenum and tungstate, and also has multi-ton production.

In oxidative-organosolvent cellulose obtaining process, citric acid can help activate oxidizing agent and ensure effective interaction with cellulose. Catalytic properties of citric acid can improve reaction rate and provide more efficient cellulose conversion. However, it is important to consider that usage of citric acid as catalyst may have limitations. First of all, it depends on specific process conditions. Therefore, optimizing acid concentration, temperature, reaction time and other parameters may be necessary to achieve optimal results.

In oxidative-organosolvent process for cellulose obtaining usage of citric acid as catalyst, the following chemical reactions take place.

1. Citric acid ($C_6H_8O_7$) splits into hydrogen ions (H^+) and citrate ions ($C_6H_5O_7I^-$):

$$C_6H_5O_7 \rightarrow H^+ + C_6H_5O_7I^-.$$

2. An oxidizing agent, which can be, for example, hydrogen peroxide (H_2O_2), splits into hydroxide ions (OH^-):

$$H_2O_2 \rightarrow 2OH^-.$$

3. Hydroxide ions react with cellulose ($C_6H_{10}O_5$) with citric acid presence, causing cellulose splitting into shorter polymer chains:

$$C_6H_{10}O_5 + nOH^- \rightarrow \left(C_6H_{10}O_5\right)_n - 1 + C_6H_{10}O_5^{-(n-1)}.$$

4. As a result, short cellulose polymer chains can be further cleaved or dissolved in solvent containing citric acid which is promote cellulose delignification.

Citric acid acts as catalyst in these reactions, accelerating cellulose oxidation and the citric acid polymerization. This contributes to improving cellulose solubility, reducing lignin content, and obtaining higher cellulose yield.

More soluble and less polluted cellulose is obtained as a result of oxidation-organosolvent process using citric acid as catalyst. This indicates possibility of its usage in paper and cardboard production.

The authors in work [3] proposed alternative method for obtaining cellulose from agricultural waste. It includes oxidative processing using wheat straw as raw material. Solution for process consists of glacial acetic acid and water in volume ratio 75:25 with addition of hydrogen peroxide as an oxidant. As delignification-process catalyst, citric acid was used. The main technological parameters were temperature and delignification duration. Thus, delignification process was carried out at temperatures from 80 to 100 ± 2°C and duration from 60 to 180 minutes. It was established that parameters increasing, especially temperature, accelerates delignification process. It allows obtain cellulose with high yield and low residual lignin content. Formation additional hydrogen bonds between polysaccharides and high hemicelluloses content are achieved by increasing processing time to 180 minutes. As a result, it leads to better papermaking properties of cellulose. Physical and mechanical properties in obtained pulp also improve slightly with increasing process duration. It can be concluded that such cellulose can be used for production different types of bleached paper [3].

Environmentally friendly method of production microcrystalline cellulose from bagasse can be showed as example of usage of non-wood plant raw materials. Process carried out by acid delignification method with preliminary alkaline treatment and further oxidation process. This process showed good yield of microcrystalline cellulose with result 310 g per 1 kg of plant material. Equally, important fact is that microcrystalline cellulose production is considered energy-intensive. For this example, it should be noted that usage of pre-treatment reduces duration of the reaction. In turn, it minimizes electricity consumption without affecting to product quality and yield. In addition, such microcrystalline cellulose was analysed using various methods and showed high-quality chemical composition and purity of samples. Therefore, such environmentally friendly method of producing microcrystalline cellulose from inexpensive, renewable and available raw materials such as bagasse is quite promising and alternative [33].

Nanocellulose has unique properties such as high surface area, aspect ratio, mechanical strength and stiffness. These properties combined with availability, biodegradability, and stability make nanocellulose good opponent for synthetic polymers. It should be noted that lignocellulosic biomass produced from agricultural and industrial waste is readily available and shows great promise as inexpensive and high-quality raw material for nanocellulose production. Source of waste does not significantly affect to main stages in process if talking about technology of nanocellulose production. Principles remain the same for all sources of waste. It is quite important that process parameters should be selected for different raw materials separately. It is connected with composition and structure of raw materials, which affect to production process. Nowadays, acid hydrolysis and oxidation with 2,2,6,6-tetramethylpiperidine-1-oxyl, which is also called TEMPO-oxidation are the most widespread methods of obtaining nanocellulose [34].

Nanocellulose widely used as addictive in cardboard and paper industry as filler to provide mechanical strength for products. Membranes based on nanocellulose have excellent mechanical properties and, as a result, they increase filters durability. Large specific surface area, high aspect ratio and broad possibilities for chemical modification are the most important advantages of nanocellulose. Nanocellulose membranes can be effective as separate product. It is currently proven that nanocellulose membranes in combination with organic or inorganic components purify most effectively [35, 36].

Current needs for purification various types of impurities in water leads to development new and innovative applications such as creation of highly efficient membranes. Cellulose fibres obtained from agriculture wastes can be used for membrane production using various methods. These materials are often considered promising alternatives for replacing and improving energy-intensive operations in many industries [37].

Membrane efficiency is dependent on material, which is used for its production. It is directly affects on its permeability, structure and thickness. Mixed-matrix membrane is one of membrane type that has attracted considerable attention. It is also called composite and obtained by direct integration of filler into the polymer matrix [38]. Both organic and inorganic material can act as filler. It is advisable and effective to use inorganic material with large number of micropores in combination with main adsorbate to achieve optimal cleaning results. For this case, using organic base and inorganic filler give possibility to apply simultaneously properties of both materials [39]. Membranes with mixed matrix demonstrate excellent mechanical strength and can be used in various industries [41]. Ways of the cellulose and fillers' modification for improving their structure are being conducted nowadays. These researches include searching methods for reducing particle size to nanosize, increasing mechanical strength and increasing access to hydroxyl groups. Various functional groups are used to modify polymers such as amine, aniline, methacrylate, polyvinyl alcohol, and polyethylene oxide [40, 41].

Cellulose-based membranes are quite effective in pressure filtration processes such as micro-, ultra- and nanofiltration. Such methods of water purification are quite simple, effective and environmentally friendly. Thus, usage of cellulose as biomass for membranes production is promising alternative to petroleum-based resins and other plastics, which commonly used in such materials.

4. CONCLUSION

It can be concluded that such developments in field of modern technologies for obtaining pulp from non-wood plant raw materials and agricultural waste using oxidative-organosolvent delignification methods are promising, but insufficiently researched. There are no comprehensive studies about usage of oxidation-organosolvent cellulose in production of thin types of paper and cellulose membranes. Its systematic development requires further scientific developments.

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