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ATTEMPTS TO CONCENTRATE AND FRACTIONATE KRAFT BLACK LIQUORS BY ULTRAFILTRATION

The kraft (sulphate) liquor, a by-product formed during cellulose-pulp production by means of sulphate method, is a valuable chemical raw material because of high lignin content. The application of ultrafiltration to the processing of waste allows separation of lignin from other low-molecular substances.

In the paper, investigations concerning ultrafiltration of black liquor using polyacrylonitrile and poly(vinyl chloride) membranes and plate-and-frame ultrafiltration module of 0.18 m² membrane area have been presented. The membranes were tested with water, dextrane solutions and raw black liquors and then the attempts to concentrate and fractionate black liquor were carried out using membranes of various compactness and various pressures. In the course of the process two fractions were obtained: the retentate with high lignin content and filtrate which contains 80% of sodium compounds.

1. INTRODUCTION

The kraft (sulphate) process, yielding as a by-product black liquors, is at present the most common method of producing paper pulp. Its expansion is due to the following advantages:

1) its adaptability to the processing of all kinds of by-products, even of poor quality;

2) extremely favourable properties of sulphate paper pulp, even if it is of rather poor quality;

3) highly effective regeneration of chemicals and heat, accompanied by a neutralization of organic wastes, thanks to which the activity of pulp mill becomes less noxious for rivers and other water reservoirs.

A drawback of this process, however, is that considerable amounts of badly smelling organic sulphur compounds are emitted by the pulp mill.

Alkalignin, further on called sulphate lignin, is nowadays used merely as a source of energy, which is obtained by combusting the concentrated liquor resulting from

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the recovery of digested chemicals and their recirculation in the production process. On the other hand, sulphate lignin is a valuable chemical raw material, which might be applied in various branches of national economy.

In some pulp mills all over the world, sulphate lignin is educed from black liquor by precipitating it by means of sulphuric acid and carbon dioxide. It has also been attempted to apply ultrafiltration for the purpose of getting macromolecular lignin from black liquors. Such a process consists in the fractionation of lignin in such a way that the retentate still contains fractions with a higher molecular mass, whereas the low-molecular fractions pass to the filtrate. Investigations carried out both in America [1] and in Europe [2] have proved that the ultrafiltration of black liquors is very profitable, indeed.

Investigations concerning the ultrafiltration of black liquors have been taken up also in the Department of Sanitary Chemistry and Membrane Processes at the Faculty of Environmental Engineering, Technical University of Silesia. The present paper deals with preliminary laboratory tests of black liquor ultrafiltration, making use of polyacrylonitrile and poly(vinyl chloride) membranes produced in this laboratory.

2. POST-DIGESTION KRAFT (SULPHATE) LIQUORS

2.1. PHYSICOCHEMICAL CHARACTERISTICS

When the sulphate method of producing chemical paper pulp is applied, the comminuted vegetable material is treated at a temperature of about 180°C with an aqueous solution, the so-called white liquor, the active components of which are sodium hydroxide and sodium sulphide. The post-reaction liquid, the so-called black liquor, is separated from the basic product (paper pulp) in the course of rinsing.

Black liquor contains dissolved organic substances as well as inorganic ones. The former comprise a part of unreacted sodium hydroxide and sulphide as well as inactive components contained in white liquor (sodium carbonate, sodium sulphate, etc.). Inorganic compounds are usually determined in the liquor as ash resulting from the combustion of a dried sample of black liquor, which is possibly acidified with sulphuric acid. Therefore, the sodium bounded with the phenol and carboxyl groups of organic compounds is often considered to be an inorganic compound. The sodium contained in the ash occurs in the form of carbonate, and in sulphate ash – in the form of sodium sulphate.

The essential organic components of black liquor are thiolignin, called sulphate lignin, aliphatic acids as well as hydroxy acids and their lactones. The first of these components is formed in the course of the digestion of wood from native lignin as a result of the hydrolysis of intramolecular ether bonds and the degradation of the molecule. BOGOMOLOV [3] provides the following empirical formula of alkathiolignin:

$$\begin{array}{l} (OCH_3)_4- \\ (CO)_2 \quad - \\ COOH \; - \end{array} \left[C_{47} H_{37} O_2 S \right] \begin{array}{l} -(OH)_4 \quad \text{phenol and enol} \\ -(OH)_2 \quad \text{alcoholic} \end{array}$$
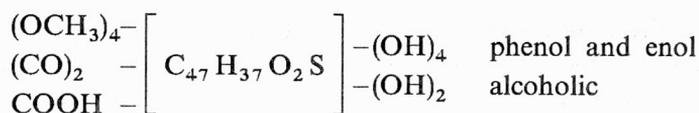
In comparison with native lignin, it contains fewer methoxyl groups (13% instead of 16%), because they have been subjected to hydrolysis in the course of digestion. Therefore, its content of phenol groups is considerably higher (1% instead of 0.3%). In result of its reaction with sodium sulphide lignin, present in white liquor, sulphate lignin contains 1–3% sulphur in the form of sulphoxide (R_1–SO–R_2) and sulphone (R–SO_2) groups. The presence of thioether bonds (R_1–S–R_2) cannot be excluded [4].

In the course of digestion, carbohydrates – in particular those with a low degree of polymerization, called hemicellulose – are subjected to an alkalic hydrolysis of the beta-glycoside bond connecting the monomers into a chain, or to the disintegration (splitting off) of the final links of the chain. The products of these reactions are salts of aliphatic and hydroxy acids and their lactones, as well as small amounts of acetic and formic acids [4]. Black liquor contains also small amounts of sodium salts of fatty acids and resins contained in wood.

The content of total solids in unconcentrated black liquor depends on the way in which the paper pulp is being rinsed. Usually it amounts to 16–20%. If the most modern appliances are used, a value of 30% might be achieved [5].

Table 1

Composition of typical black liquor resulting from the digestion of pine wood [6] (total solids: 20%, pH ca. 11)

Components	Content in reaction to total solids (%)
Sulphate lignin	41
Hydroxy acids and lactones	28
Acetic acid	5
Formic acid	3
Resinous and fatty acids	3
Methanol	1
Sulphur	3
Sodium	16

Due to the residual content of sodium hydroxide, black liquor is strongly alkaline, with a pH exceeding 11.

The composition of the total solids of black liquor depends to a high extent on the kind of the wood digested and the technique applied. Thus, the data reported by various authors show considerable differences. In table 1, there have been gathered

data concerning the composition of typical black liquor according to SARKANEN and
LUDWIG [6]. KIN's data [7] comply with the content of the products of the
decomposition of hydrocarbons in black liquor, though the content of lignin has
been determined by this author as being equal to 54.3%.

2.2. THE MANAGEMENT OF BLACK LIQUORS

Both from the economical and the technological view-points the assumption that
neither the inorganic nor the organic components of black liquor can be economical-
ly managed is not acceptable. Therefore the management of black liquor with the
purpose of regenerating chemical substances constitutes an integral part of the
production of paper pulp by means of the sulphate method. Figure 1 presents
a diagram of the regeneration of chemicals making use of the classical method. The
black liquor washed out from the paper pulp is concentrated in a multi-stage
evaporator, the final concentration of the total solids amounting to about 55%.
Next, it is being concentrated in direct evaporators or in specially constructed
thickeners, reaching a concentration of about 60–68%. In order to supplement the
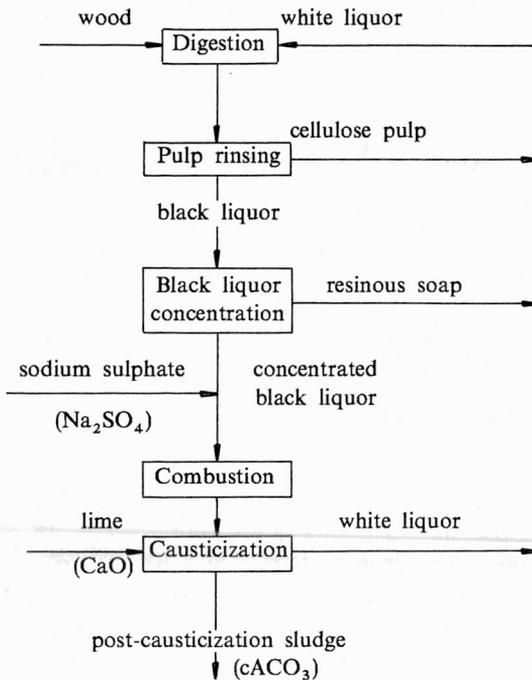
Fig. 1. Diagram of the circulation of chemicals in a sulphate paper-mill
(addition of anhydrous sodium sulphate for replenishing the losses of chemicals)

losses of chemicals, anhydrous sodium sulphate is added to this concentrated liquor, and then combusted in a so-called sodium boiler. Because of its content of organic substance, concentrated black liquor has a calorific value of about 8500 kJ/kg, so that in can be burned without applying any additional fuel. The sodium salts contained in the combusted liquor melt due to the temperature existing in the combustion chamber (about 1150°C). From the boiler they flow out as a so-called alloy into a container. As the alloy dissolves in the so-called weak white liquor (by-product in the process of causticization), the so-called green liquor, containing mainly sodium carbonate and sulphide, is formed. This liquor is used for the digestion of wood.

Table 2

Thermal balance of a sulphate paper-mill [4]

Item	Thermal energy MJ/t		
	Minimum	Mean value	Maximum
Heat generated in the regeneration boiler	11300	12350	13200
Heat used to evaporate black liquor	3000	3000	3000
Heat used for digestion	3400	4450	6950
Total	6400	7450	9950
Heat used to dry the paper-pulp	2850	3600	4050
Overall values	9250	11050	14000

In the regeneration boiler, high-pressure steam is generated for the plant's power station, and after this steam has been partly expanded, it is also used for technological purposes. As RYDHOLM's data [4] indicate, the steam resulting from the combustion of black liquors may easily cover the demand for thermal energy of the pulp mill (table 2). In paper mills, in which the pulp is used on the spot, there is no need to dry it. In this case, a considerable surplus of steam generated in the sodium boiler can be utilized in the paper-mill itself.

The lignin contained in the black liquor is a valuable chemical raw material, which may be used for the production of dispersing agents, dyes, auxiliary drilling agents, synthetic rubber, floculating agents and mainly-binding agents with differentiated properties [8].

Although the sulphate method cannot be applied to the production of paper-pulps without regenerating the chemicals used, which requires the utilization of the organic components of the liquor as the fuel, it is still possible to reserve some

amount of lignin for other purposes. The essential problem in the case of retrieving a certain part of lignin from black liquor is the effect of this operation on its usability as fuel for regenerating boilers, because the content of lignin determines, besides the content of product resulting from the degradation of hydrocarbons, the calorimetric value of the liquor. It is, however, possible to retrieve about 38 kg of lignin per ton of the pulp produced without depriving the concentrated liquor of its ability to be combusted [3]. The retrieval of some part of lignin from the liquor limits also the necessity of achieving the proper heat release of the boiler, because the boiler ought to be supplied with enough fuel, so that the amount of thermal energy generated in the course of one hour would exceed 380 MJ/m^3 [3] of the volume of the combustion chamber in mean-value units, e.g. installed in the paper mills at Ostrołęka and Krapkowice. Thus, lignin can be retrieved only in paper mills in which the amount of produced pulp warrants a heat release of the regenerative boiler. This might be very profitable because, in addition to valuable raw material, i.e. sulphate lignin, the possibility arises to produce additional amounts of pa-per-pulp at very low costs and without any larger investments [2].

Sulphate lignin can be obtained by adjusting the pH value of black liquor. At pH = 9 it is precipitated in the form of sodium salt, and pH = 2.5 – in its free form. In order to acidify it, the carbon dioxide contained in flue gases or sulphuric acid is used.

Recently also ultrafiltration has been applied in the processing of black liquors. The separation of lignin from black liquor by means of ultrafiltration is accompanied by fractionation. In the retentate fractions with a higher molecular mass remain, those with a lower molecular mass being in the filtrate. The product obtained in this way is characterized by a worse chemical purity than that precipitated by acid, but it contains macromolecular lignin, which is of great advantage for many applications. Ultrafiltration is possible in either of the two cases: the black liquor is soap-skimmed before being concentrated or it is concentrated up to about 30% total solids and soap-skimmed. In the case of ultrafiltration of soap-skimmed liquor, it should be previously diluted with water, which will have to be evaporated as a filtrate combined with the black liquor that had not been subjected to ultrafiltration. This, however, makes it possible to avoid losses of resin soaps, from which tall oil is produced.

3. EXPERIMENTAL AND RESULTS

3.1. APPARATUS AND MEMBRANES

For ultrafiltration of black liquors (resulting from the digestion of wood by means of the sulphate method) and the testing of membranes an installation was used, the main element of which was a large-scale laboratory module produced in

Denmark by the Danske Sukkerfabrikker (DDS). Schematically this installation has been shown in figure 2. The plate-frame module is provided with flat membranes with a surface area of 0.19 m², divided into five equal sections. The concentrated liquid flows through narrow channels, 0.5 mm high, and the permeate is drained off separately from each section.
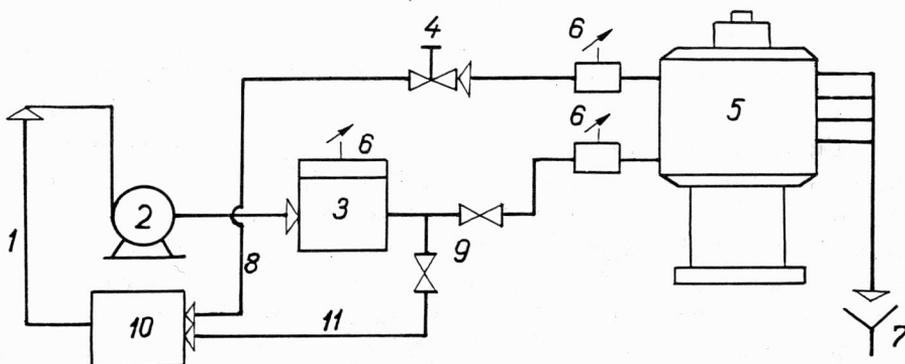

Fig. 2. Ultrafiltration installation used in the investigations
1 – inlet of black liquor, *2* – pump, *3* – pressure buffer, *4* – pressure reducing valve,
5 – ultrafiltration module, *6* – manometer, *7* – outlet of permeate, *8* – outlet of retentate,
9 – cut-off valve, *10* – black liquor tank, *11* – by-pass

Table 3

Composition of casting solutions and conditions of membrane preparation

Composition of casting solutions and conditions of membrane preparation	Type of membrane			
	PAN-15	PAN-17.5	PAN-20	PVC-12
Composition of casting solutions (% mas.):				
polyacrylonitrile	15	17.5	20	–
poly(vinyl chloride)	–	–	–	12
N, N-dimethylformamide	85	82.5	80	88
Temperature of casting solution (°C)	22	22	22	25
Gelation temperature (°C)	22	22	22	5
Time of gelation (h)	0.25	0.25	0.25	0.25

In our investigations, flat asymmetric polyacrylonitryle (PAN) and poly(vinyl chloride) (PVC) membranes were used. In order to obtain PAN-membranes, non-mat man-made fibres from the fibre plant Chemitex-Anilana in Łódź were used as raw material. PVC-membranes are made from a polymer that is obtained by means of the suspension method, called Tarnwinyl S-64, coming from the Nitrogen Plant in Tarnów.

All kinds of membranes are produced by means of the phase-inversion method [9], [10]. In such a method, the polymer solution in dimethylformamide is cast and then gelated in a non-solvent (water) to form a film. In table 3 some data concerning the composition of the binary film generating solutions as well as the conditions for the preparation of membranes have been gathered.

3.2. CHARACTERISTICS OF THE MEMBRANES APPLIED

Before the investigations, each set of membranes was tested and conditioned. This process consisted in passing successively through the membranes the following liquids: distilled water, raw liquor and aqueous solutions of dextrane preparations from "Polfa" at Kutno. The molecular mass of the dextranes applied amounted to 3,000, 40,000, 80,000 and 110,00, their concentration being 1 kg/m^3. In the case of PAN membranes, distilled water was passed through them for 12 hours (at pressures of 0.4, 0.5, and 0.6 MPa), liquor – for 9 hours (at pressures as above), and again distilled water – for 4 hours (at a pressure of 0.5 MPa). Thereafter the dextrane preparations were passed (for 2 hours at a pressure of 0.5 MPa each). The time of testing and conditioning PVC membranes was the same, but lower pressures were applied: water and liquor at 0.2, 0.4 and 0.5 MPa, dextranes at 0.4 MPa. The working pressure for these tests was chosen basing on the previous experiments with the same kinds of membranes [11]–[15]. The aim of these tests was to determine the permeability of the membranes produced and the retention coefficients of dextrane preparations, calculated in result of analyses of the permeate and raw solution, with respect to sugar content in a liquid. Analyses were carried out according to Bertrand's method [16]. The volumetric permeate flux and water flux were calculated basing on measurements of the liquid volume passing through the membrane.

Table 4

Volumetric water flux obtained by passing the liquid
through PAN and PVC ultrafiltration membranes

Kind of membrane	Volumetric water flux m^3/m$^2 \cdot$ d			
	$\Delta P = 0.2$ MPa	$\Delta P = 0.4$ MPa	$\Delta P = 0.5$ MPa	$\Delta P = 0.6$ MPa
PAN-15	–	3.93	5.01	4.60
PAN-17.5	–	3.69	4.04	4.78
PAN-20	–	2.735	3.17	3.78
PVC-12	2.495	3.315	3.23	–

Volumetric permeate flux obtained during ultrafiltration
of black liquor on PAN and PVC membranes

Kind of membrane	Volumetric permeate flux $m^3/m^2 \cdot d$			
	$\Delta P = 0.2$ MPa	$\Delta P = 0.4$ MPa	$\Delta P = 0.5$ MPa	$\Delta P = 0.6$ MPa
PAN-15	–	0.569	0.632	0.639
PAN-17.5	–	0.638	0.702	1.07
PAN-20	–	0.649	0.751	0.833
PVC-12	0.525	0.636	0.708	–

Permeate flux (J_v) and retention coefficient (R)
of dextrane preparations for PAN membranes (pressure: 0.5 MPa)
and PVC membranes: (pressure: 0.4 MPa), dextrane concentration: 1 kg/m³

Molecular mass of the dextrane	PAN-15		PAN-17.5		PAN-20		PVC-12	
	J_v m/d	R %	J_v m/d	R %	J_v m/d	R %	J_v m/d	R %
3000	1.71	37.3	3.27	62.6	1.41	36.0	1.42	64.0
40000	1.39	38.5	2.76	69.9	1.305	83.7	1.33	80.7
80000	1.13	92.2	2.08	94.3	1.29	95.8	1.27	88.5
110000	0.934	96.8	1.76	97.2	1.15	98.0	1.18	89.2

The membranes were tested with raw liquor in order to condition the respective sets of membranes and to determine the permeate flux with the purpose of achieving its proper concentration. All these tests were carried out making use of batch non-concentration mode, i.e. the filtrate obtained was recycled to the tank after having taken a sample for an analysis.

Tables 4–6 display the full characteristics of the membranes obtained. The permeability of the membranes increases with pressure. The efficiency and selectivity of a membrane depend on its permeability. As investigations have shown, PAN-15 and PAN-17.5 membranes retain nearly all the dextrane particles with a molecular mass exceeding 80,000, while PAN-20 and PVC-12 membranes retain particles with a molecular mass above 40,000. Thus, it may be assumed that the "cut off" for PAN-15 and PAN-17.5 membranes amounts to about 80,000, and for PAN-20 and PVC membranes – to about 40,000. While the membranes were being tested with raw liquor at a pressure changing within the range from 0.4 to 0.6 MPa, it has been

found that the permeate flux increases. In the case of PAN-15 membranes this increase amounted to 22%, in the case of PAN-17.5 membranes – to about 67%, and in the case of PAN-20 membranes – to about 28%. In the case of PVC-12 membranes the increase of the permeate flux amounted to about 35% at pressures within the range from 0.2 to 0.5 MPa.

3.3. CONCENTRATION AND FRACTIONATION OF BLACK LIQUORS

Attempts to concentrate black liquors not soap-skimmed by means of ultrafiltration and to fractionate them have been made with all the four kinds of membranes. For this purpose, post-sulphate liquors from the paper-mill at Kalety were used. Samples of this liquor were taken in the paper-mill from the surge chamber before its preliminary concentration (which leads to the removal of resin-soaps and tall oil from liquors). Before the black liquor was introduced into the system investigated, it was filtered through a ceramic strainer with a diameter of about 20 μm in order to remove all mechanical contaminations, particularly cellulose fibres.

The process of concentrating and fractionating the liquor was accomplished by means of the batch-concentration mode, in the course of which the liquor was recycling until the required flow yield of the permeate was reached, viz. in each case 80% (20 dm^3 of liquor yielded 4 dm^3 of retentate and 16 dm^3 of permeate). Due to extensive foaming of the liquor in the case of PVC membranes, these volumes had to be slightly increased (25 dm^3 of permeate and 5 dm^3 of retentate). The efficiency of the process was determined by measuring the permeate recovery time, and the permeate flux was calculated in the course of concentration. In order to control the efficiency of the process in the respective fractions, i.e. the permeate, retentate and raw liquor, the contents of the dissolved organic and mineral substances as well as the contents of the lignin compounds and sodium were analysed. The content of lignin compounds was measured by means of the spectrophotometer Specord M-40 within the ultraviolet range. The absorbance of the sample tested was determined and referred to the previously prepared calibration curve. The content of sodium was measured by means of the photometer Flapho-4. The total solids as well as the contents of organic and mineral substances were determined gravimetrically.

Tables 7–10 contain the results obtained in the course of concentrating the black liquor on all the membranes applied at various working pressures, which in the case of polyacrylonitryle membranes amounted to 0.5, 0.75 and 1.0 MPa, and in the case of the PVC-12 membrane – 0.3, 0.4 and 0.5 MPa, respectively. In the course of each test, the permeate flux decreased with the increase in concentration of the liquors due to increase in the concentration of substances dissolved in the retentate. The growth of the pressure brings about two phenomena: the com-

Table 7

Efficiency of the ultrafiltration concentration and fractionation
of black liquor on a PAN-15 membrane
(membrane area: 0.18 m², permeate flow yield: 0.8, feed rate: 500 dm³/h)

Process efficiency	Liquor kg/m³	Permeate kg/m³	Retentate kg/m³	Retention coefficient %
Pressure: 0.5 MPa; average permeate flux: 0.407 m³/m²·d				
Dissolved substances	130	95.5	199	26.55
Organic compounds	58.6	42.7	133	27.2
Mineral compounds	71.4	52.8	64.2	26.0
Lignin compounds	51.5	35.9	112	30.3
Sodium	16.0	15.5	19.5	3.12
Pressure: 0.75 MPa; average permeate flux: 0.586 m³/m²·d				
Dissolved substances	118	88.7	321	24.5
Organic compounds	55.4	34.7	149	37.3
Mineral compounds	63.5	54.1	72.1	14.7
Lignin compounds	50.9	33.45	122	34.2
Sodium	16.3	15.0	22.5	7.90
Pressure: 1.0 MPa; average permeate flux: 0.505 m³/m²·d				
Dissolved substances	119	90.1	212	24.4
Organic compounds	53.7	34.0	137	36.8
Mineral compounds	65.5	56.1	74.9	14.3
Lignin compounds	51.8	31.9	128	38.4
Sodium	16.0	14.5	21.0	9.40

pression of pores in the membranes and the opening of new pores. Within the range of the pressures applied the latter effect is dominant (with only one exception), so that the average permeate flux increases with the increase in pressure, this increase amounting to 10–23%.

As a result of ultrafiltration concentration of black liquors, two fractions, differing in their contents of dissolved substances, are obtained. The value of the retention coefficient of the substances dissolved, determined by means of the following formula:

$$R = \frac{C_l - C_p}{C_l},$$

where C_l denotes concentration of substances dissolved in a liquor, and C_p is concentration of substances dissolved in a permeate, was not very high, ranging in the case of all the tests from 20 to 27%. The ratio of the concentration of substances

Efficiency of the ultrafiltration concentration and fractionation
of black liquor on a PAN-17.5 membrane
(membrane area: 0.18 m^2, permeate flow yield: 0.8, feed rate: 500 dm^3/h)

Process efficiency	Liquor kg/m^3	Permeate kg/m^3	Retentate kg/m^3	Retention coefficient %
Pressure: 0.5 MPa; average permeate flux: 0.509 m^3/m$^2 \cdot$ d				
Dissolved substances	125	93.4	232	25.3
Organic compounds	54.2	33.3	159	38.5
Mineral compounds	68.1	60.1	73.3	11.8
Lignin compounds	50.9	31.8	131	37.5
Sodium	15.9	15.0	21.5	5.60
Pressure 0.75 MPa; average permeate flux: 0.703 m^3/m$^2 \cdot$ d				
Dissolved substances	121.5	93.2	215	23.2
Organic compounds	54.6	35.9	144	34.2
Mineral compounds	66.7	57.4	70.9	13.9
Lignin compounds	49.9	31.8	115.5	36.2
Sodium	16.2	15.5	19.0	4.30

dissolved in the lignin concentrates (retentates) to their concentration in the liquor varied within the range of 1.6–1.9. There is no linear dependence between the pressure increase and the changes in the concentration of the substances dissolved in the concentrates obtained. The irregular character of these changes is doubtlessly connected with changes in the inner structure of the mambranes due to the increase of pressure. It seems that black liquors ought to be concentrated and fractionated at a pressure ranging from 0.5 to 0.7 MPa.

The fact that the retention coefficient of lignin compounds is higher than that of dissolved substances is of considerable importance. This means that in comparison with raw liquor the retentate is much richer in macromolecular lignin fractions. In most tests that have been carried out, the retention coefficient of lignin compounds lies between 35 and 40% (the highest value was obtained in the case of the PAN-20 membrane at a pressure of 1.0 MPa, and amounted to 41.6%). The ratio of the content of lignin compounds in the concentrates obtained to their content in raw liquor in each case exceeded 2, ranging from 2.17 to 2.57. The highest ratio was characteristic of the PAN-17.5 membrane (lignin concentration in the retentate – 131 kg/m^3, in the liquor – 50.9 kg/m^3). The retentate, whose volume is only 20% of the initial volume of the liquor, contains about 45 to 50% of the total amount of lignin introduced to the liquor where ultrafiltration occurs.

Table 9

Efficiency of the ultrafiltration concentration and fractionation
of black liquor on a PAN-20 membrane
(membrane area: 0.18 m², permeate flow yield: 0.8, feed rate: 500 dm³/h)

Process efficiency	Liquor kg/m³	Permeate kg/m³	Retentate kg/m³	Retention coefficient %
Pressure: 0.5 MPa; average permeate flux: 0.604 m³/m²·d				
Dissolved substances	120	97.6	200	18.6
Organic compounds	54.0	40.2	127	25.5
Mineral compounds	65.9	57.4	72.4	12.8
Lignin compounds	51.3	32.9	115.5	35.9
Sodium	19.0	18.5	20.0	3.12
Pressure: 0.75 MPa; average permeate flux: 0.785 m³/m²·d				
Dissolved substances	121	95.6	216	20.8
Organic compounds	54.5	36.9	158	32.3
Mineral compounds	66.5	58.6	78.3	11.8
Lignin compounds	50.8	31.9	121	37.2
Sodium	18.3	17.0	19.0	7.10
Pressure: 1.0 MPa; average permeate flux: 0.649 m³/m²·d				
Dissolved substances	119	94.4	206	20.9
Organic compounds	53.6	38.5	134	28.2
Mineral compounds	65.8	55.9	72.1	15.0
Lignin compounds	49.8	29.3	112	41.6
Sodium	16.0	15.7	17.5	1.90

A measure of the enrichment of this retentate with lignin is the ratio of the lignin content to the total content of dissolved substances. In raw liquor it amounts to about 0.41–0.43, whereas in the lignin concentrate it is 0.54–0.60, which indicates a considerable enrichment of the retentate with lignin compounds.

A very important component is sodium, as far as the separation of sulphate lignin by means of ultrafiltration of the liquor is concerned. It has been found that it easily passes through ultrafiltration membranes, and its retention coefficient is rather small, below 10%. This is a favourable phenomenon, as the permeate originating during ultrafiltration of liquors can be returned and utilized in the production process in the paper-mill, where – after the regeneration of chemicals in the sodium boiler – all the losses have to be replenished. It has been calculated that the total amount of sodium passing into the permeate fraction is in the case of all the tests performed within the range of 72.5–82.5%.

Table 10

Efficiency of the ultrafiltration concentration and fractionation
of black liquor on a PVC-12 membrane
(membrane area: 0.18 m^2, permeate flow yield: 0.8, feed rate: 500 dm^3/h)

Process efficiency	Liquor kg/m^3	Permeate kg/m^3	Retentate kg/m^3	Retention coefficient %
Pressure: 0.3 MPa; average permeate flux: 0.398 m^3/m$^2 \cdot$d				
Dissolved substances	142	116	230	18.3
Organic compounds	67.4	49.4	149.5	26.7
Mineral compounds	74.6	66.6	80.3	10.7
Lignin compounds	59.4	39.1	134.5	34.1
Sodium	19.0	14.0	16.4	3.12
Pressure: 0.4 MPa; average permeate flux: 0.522 m^3/m$^2 \cdot$d				
Dissolved substances	140	116	221	16.9
Organic compounds	66.4	46.8	144	29.5
Mineral compounds	73.5	69.5	77.3	6.40
Lignin compounds	59.8	38.1	130	36.3
Sodium	14.0	13.0	16.2	7.10
Pressure: 0.5 MPa; average permeate flux: 0.573 m^3/m$^2 \cdot$d				
Dissolved substances	143	113	233	21.0
Organic compounds	67.8	45.8	154.5	32.4
Mineral compounds	75.0	66.9	78.3	10.8
Lignin compounds	60.0	39.2	139	34.6
Sodium	14.4	13.1	16.1	9.00

Neither has any considerable influence (besides the pressure) of the compactness of PAN membranes on the results of the fractionation and concentration of black liquors been detected. Thus, taking into consideration the mechanical resistance of the membranes as well as the test results obtained, it is feasible to apply more compact membranes.

Similar results of concentrating and fractionating black liquors have been achieved in the case of PVC membranes, although they seem to be less favourable than those obtained on PAN membranes.

4. CONCLUSIONS

1. Polyacrylonitrile membranes with a permeability of water of about 4–5 m^3/m$^2 \cdot$d (at a pressure of 0.5–0.6 MPa) may be successfully applied to concentration

and fractionation of black liquors which are formed during digestion of wood by means of the sulphate method.

2. In the course of the process, two fractions are obtained: the retentate (concentrate) and the permeate (filtrate), differing from each other in the content of dissolved substances and other compounds which are important from the viewpoint of the regeneration of the liquor, i.e. lignin compounds and sodium.

3. About 80% of sodium compounds pass into the permeate fraction and can be recycled in the production process.

4. The retentate fraction contains about 50% of initial amount of lignin compounds with a higher concentration than that of raw liquor.

5. The purity of the lignin fraction amounts to about 0.6, which means that in the total solids of the retentate there are 60% of pure lignin compounds.

6. In order to enrich the retentate with lignin compounds, the ultrafiltration process of concentration and fractionation ought to be carried out by means of dilution mode (diafiltration), i.e. the retentate is to be diluted with water and returned to ultrafiltration.

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PRÓBY ZATĘŻANIA I FRAKCJONOWANIA
SIARCZANOWYCH ŁUGÓW POWARZELNYCH METODĄ ULTRAFILTRACJI

Ług czarny (siarczanowy), produkt uboczny powstający w siarczanowym procesie wytwarzania mas celulozowych, jest wartościowym surowcem z powodu dużej zawartości związków ligninowych. Zastosowanie ultrafiltracji w przerobie tego odpadu umożliwia oddzielenie związków ligninowych od innych substancji małocząsteczkowych.

Przedstawiono wyniki badań nad ultrafiltracją ługu czarnego przez membrany z poliakrylonitrylu i poli(chlorku winylu) oraz ultrafiltracyjnego modułu płytowo-ramowego o powierzchni membran 0,18 m². W eksperymentach użyto wodę, roztwory dekstranów i surowy ług czarny. Przeprowadzono próby zatężania i frakcjonowania ługu czarnego, stosując w tym celu membrany różniące się zwartością oraz różne ciśnienia. W trakcie procesu otrzymano dwie frakcje: retentat o wysokim stężeniu związków ligninowych i filtrat zawierający 80% związków sodu.

ПРОБЫ КОНЦЕНТРАЦИИ И ФРАКЦИОНИРОВАНИЯ
ПОСЛЕВАРОЧНЫХ СУЛЬФАТНЫХ ЩЕЛКОВ МЕТОДОМ УЛЬТРАФИЛЬТРАЦИИ

Черный (послеварочный) щелок, побочный продукт, образующийся в сульфатном процессе изготовления целлюлозы, является важным сырьем из-за большего содержания лигнинных соединений. Применение ультрафилтрации в переработке этого отброса дает возможность разделения лигнинных соединений от других маломолекулярных веществ.

Представлены результаты исследований ультрафилтрации черного щелка через мембраны из полиакрилнитрила и поли(винил хлорида), а также ультрафилтрационного плитого-рамочного модуля поверхности мембран 0,18 м². В экспериментах употребили воду, растворы декстранов и сырый черный щелок. Проведены пробы концентрации и фракционирования черного щелка с применением для этого мембран, отличающихся плотностью, а также разных давлений. Во время процесса были получены две фракции: ретентат большей концентрации лигнинных соединений и фильтрат, содержащий 80% соединений натрия.