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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Improvement of the Technology for Reprocessing Black Liquors from Kraft Pulp Production

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Abstract—A way to improve the kraft pulp production process via acid–base treatment of black liquor was suggested. Data on the process for kraft lignin production by the sulfuric acid procedure were substantiated.

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The existing procedure for kraft pulp production is characterized by high environmental hazard and low power efficiency [1]. Black liquor reprocessing followed by recovery of alkalis deteriorates the quality of the environment. This drawback of the process is often the cause of decommissioning of pulp plants. Therefore, this process requires improvement.

One of the main distinctive features of the process that we suggest is removal of lignin and other organic compounds before evaporation of weak black liquor.

Two methods for lignin precipitation are known: treatment with sulfuric acid and with carbon dioxide [2]. The carbon dioxide method is based on acidification of black liquor with carbon dioxide:

$$\mathrm{NaO{-}R{-}COONa} + \mathrm{CO_2} + \mathrm{H_2O} \rightarrow \mathrm{HO{-}R{-}COOH} + \mathrm{Na_2CO_3}.$$

In the carbon dioxide method for precipitation of organic compounds, their yield does not exceed 30%. The yield of organic compounds can be increased to 70% by saturation of the black liquor with carbon dioxide under pressure. The authors of [3] suggest a procedure for black liquor treatment with carbon dioxide present in flue gases from decarbonization furnaces. However, the process implementation is thus complicated. By carbon dioxide treatment, it is possible to recover organic compounds when large circulation streams of the black liquor are organized. The soda recovery boiler (SRB) as the main source of capital and power expenditures can be eliminated from the chain of the apparatuses. However, problems of the power efficiency and environmental safety of the technology in the lime decarbonization process are not solved. Preservation of lime as the agent for caustization of the soda solution in the carbon dioxide process gives rise to problems in the course of solution evaporation. Sodium sulfates and carbonates and calcium sulfates formed in the process incrust the heat-exchange surface at elevated temperatures, decreasing the efficiency of the black liquor evaporation.

Sulfuric acid as a strong acid allows more complete precipitation of lignin from black liquor:

$$\mathrm{NaO{-}R{-}COONa} + \mathrm{H_2SO_4} \rightarrow \mathrm{HO{-}R{-}COOH} + \mathrm{Na_2SO_4}.$$

A process for recovering organic compounds, based on treatment of black liquor with sulfuric acid to pH 4, has been developed [4].

However, this procedure has limitations with respect to the amount of the black liquor being treated. This is apparently caused by the following factors: (1) large amounts of sodium sulfate are formed, and the sodium sulfate stream is difficult to convert to demanded products having the price sufficient for the process to be profitable; (2) the demand for lignin as filler is limited.

Thus, the suggested approaches do not solve the problems of power efficiency and environmental safety of black liquor reprocessing.

This study was aimed at improving the process and determining the optimum parameters of the sulfuric acid procedure for recovering organic compounds from the total black liquor stream in kraft pulp production. With this technology, organic compounds are taken off from the process and, after additional treatment, used as environmentally safe fuel with increased heat of combustion, demanded by consumers. The product can also be used as a raw material and in production of other demanded materials (e.g., fillers) having acceptable price. The suggested flowsheet for black liquor reprocessing is shown in Fig. 1.

In this procedure, industrial black liquor (with possible addition of anthraquinone) is acidified with sulfuric acid, and two products are obtained: lignin suspension and gaseous substances. The lignin suspension is filtered. The lignin after the filtration is washed and dried in a drier. The lignin mother liquor is neutralized with a KOH solution to pH 7–8, which is determined by the possibility of using evaporators fabricated from common carbon steel.

The neutralized solution is evaporated in an evaporator. In the first step, the solution is evaporated to reach the saturation concentration for sodium and potassium salts. The concentrated solution is then fed to the second step of evaporation, where it is concentrated to obtain a suspension with the liquid to solid weight ratio of 3–5. This ratio is determined by the requirements to the evaporator operation, namely, by the need to exclude plugging of boiling pipes.

The resulting suspension of alkalis after the second concentration step is separated by filtration into two products: mother liquor, which is then mixed with the solution fed to the second step, and solid product of potassium and sodium sulfates.

The lime decarbonization is eliminated from the flowsheet. Therefore, the fuel supply from an external source is also eliminated. The problems of the environment protection and power saving are thus solved. Diversification of the production process is ensured, as wider range of demanded products with high consumer cost is produced. The environmental safety problems are solved for all the steps of the black liquor reprocessing.

EXPERIMENTAL

The goal of this study was to determine the optimum process parameters for recovering organic compounds suitable as fuel from the black liquor in the kraft pulp production.

Demin [4] recommends the following process parameters as optimum for lignin precipitation: liquor temperature 60–65°C and pH of the reaction mixture at the reactor outlet 4.0–4.5. However, the recommended parameters do not meet the requirements to the yield of organic compounds, and additional studies are therefore required.

The following parameters were varied in the experiment: sulfuric acid (83% concentration) amount, g dm^{-3}; reaction time, min; and anthraquinone concentration, ppm.

As starting black liquor we took the solution at the boiler outlet with 10% concentration (counting on absolutely dry matter). Anthraquinone was used as a catalyst for recovering organic compounds from the black liquor. As anthraquinone sample we used the product obtained by benzene acylation [5]. The target function of the experiment was the dependence of the yield of combustible organic compounds on the chosen varied parameters.

For performing the experiment, we chose the rotatable central composite design [6]. The factor variation levels are given in Table 1.

The experimental design and the target values of the yield of organic compounds are given in Table 2.

The yield of organic compounds was determined in three points of each experiment.

In processing of the experimental results, we obtained a regression equation for the yield of organic compounds η (%) from black liquor in the form of a quadratic polynominal:

$$
\begin{gathered}
\eta = 89.5154 + 0.3115x_1 - 1.4681x_2 + 3.5280x_3 \\
- 2.6192x_1{}^2 + 0.5875x_1x_2 + 2.9125x_1x_3 - 0.3741x_2{}^2 \\
+ 4.215x^2x^3 - 0.6392x_3{}^2,
\end{gathered}
$$

where x_1, x_2, and x_3 are the varied factors in the coded values (Tables 1, 2).

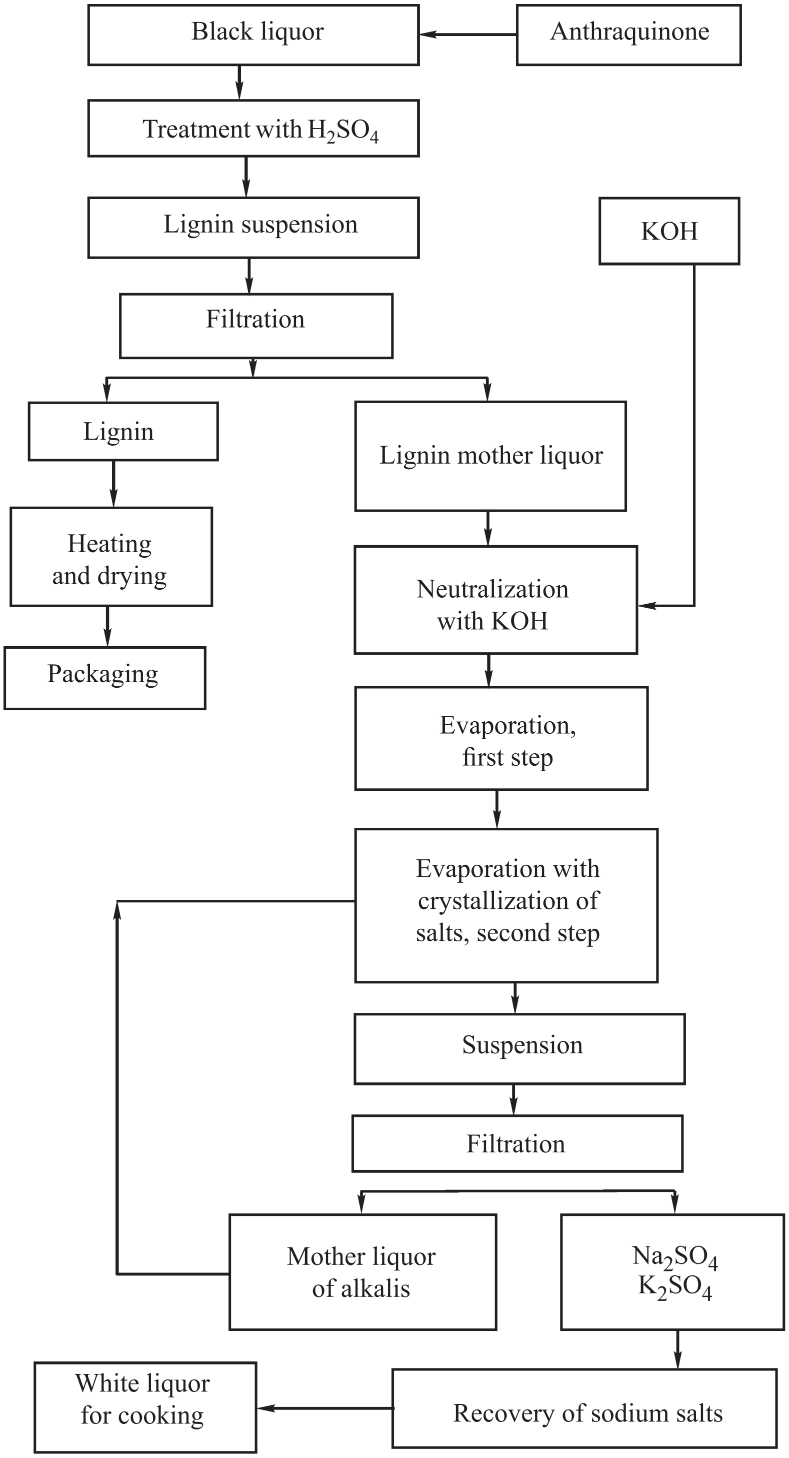

Fig. 1. Flowsheet for acid–base recovery of chemicals from black sulfate liquor.

The model adequacy was checked using Fisher's test. Because $F = 0.9637 \leq F_{cr}$ (0.05) = 2.43, the model is adequate.

As seen from Table 2, the best results were reached in run nos. 8, 12, and 13. In these experiments, the yield of organic compounds was 93–94%. Run no. 13 is characterized by the parameters more acceptable for practical operation: sulfuric acid amount 60 g dm^{-3}, anthraquinone concentration 200 ppm, and reaction time 2 min.

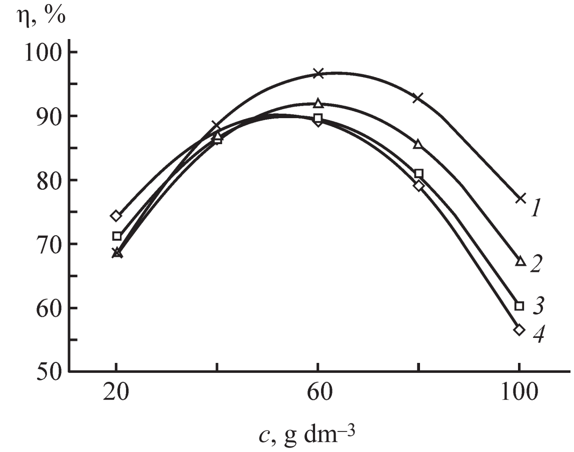

Fig. 2. Yield of organic compounds η as a function of the amount *c* of sulfuric acid fed to neutralization at different anthraquinone concentrations. Reaction time 2 min; the same for Fig. 4. Anthraquinone concentration, ppm: (*1*) 319, (*2*) 200, (*3*) 81, and (*4*) 0.

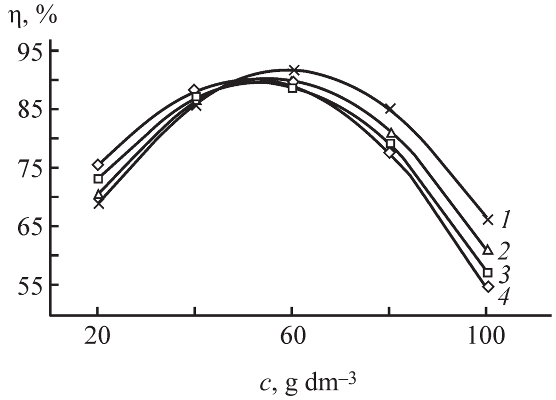

Fig. 3. Yield of organic compounds η as a function of the amount *c* of sulfuric acid fed to neutralization at different reaction times. Anthraquinone concentration $c_{\text{anthr}} = 0$ ppm; the same for Fig. 6. Reaction time, min: (*1*) 42, (*2*) 27, (*3*) 12, and (*4*) 2.

Let us consider the influence of separate variables on the yield of organic compounds. As found in the experiment (Figs. 2 and 3), at all the anthraquinone concentrations and reaction times the dependence of the yield of organic compounds on the amount of sulfuric acid fed to neutralization has a maximum corresponding to 60 g dm^{-3} H_2SO_4. At the reaction time of 2 min (Fig. 2), the maximal yield of organic compounds is reached at the anthraquinone concentration of 319 ppm, whereas at the reaction time of 42 min (Fig. 3) it is reached without anthraquinone.

The yield (Figs. 4, 5) of organic compounds increases at all anthraquinone concentrations, except the experiments at 20 g dm^{-3} H_2SO_4 (Fig. 4). The maximal yield of organic compounds from the solution is reached at 60 g dm^{-3} H_2SO_4. An increase in the anthraquinone concentration leads to shorter reaction times and higher yields of organic compounds.

The yield of organic compounds from the black liquor depends on the reaction time and sulfuric acid consumption (Figs. 6, 7). As noted above, the maximal yield is reached at the sulfuric acid amount of 60 g dm^{-3} and reaction time of 42 min. The yield of organic compounds increases with the reaction time at sulfuric acid amounts $c \geq 40$ g L^{-1}, whereas at lower H_2SO_4 amounts the yield decreases with time (Fig. 6). The presence of anthraquinone also influences the yield of organic compounds. The maximal yield is observed at the reaction time of 2 min and maximal anthraquinone dosage, 400 ppm (Fig. 7).

The experimental data allow a conclusion that the optimum parameters for recovering organic compounds are as follows: sulfuric acid (83%) amount 60 g dm^{-3},

Table 1. Factor variation levels

Factor	Code designation	Star points $x_i = -1.682$	Lower level $x_i = -1$	Base level $x_i = 0$	Upper level $x_i = +1$	Star points $x_i = +1.682$
Sulfuric acid amount, g dm^{-3}	x_1	26	40	60	80	94
Anthraquinone concentration, ppm	x_2	0	81	200	319	400
Reaction time, min	x_3	2	12	27	42	52

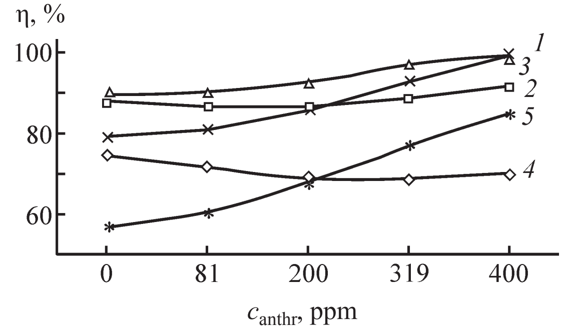

Fig. 4. Yield of organic compounds η as a function of the anthraquinone concentration c_{anthr} at different amounts of sulfuric acid taken. Sulfuric acid amount, g dm^{-3}: (*1*) 60, (*2*) 40, (*3*) 80, (*4*) 20, and (*5*) 100.

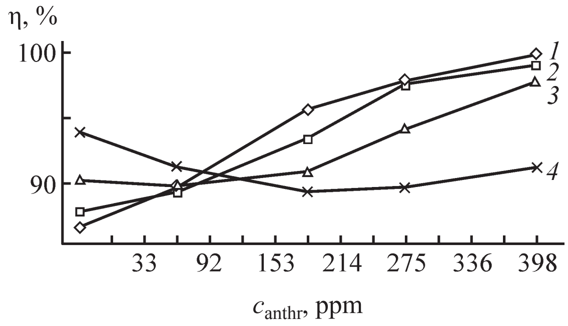

Fig. 5. Yield of organic compounds η as a function of the anthraquinone concentration c_{anthr} at different reaction times. Sulfuric acid amount 60 g dm^{-3}; the same for Fig. 7. Reaction time, min: (*1*) 2, (*2*) 12, (*3*) 27, and (*4*) 42.

Table 2. Experiment design in coded and natural variables

Level	Run no.	Design matrix			Recovery of organic compounds, %		
		x_1	x_2	x_3	1	2	3
Design core	1	–1/40	–1/81	–1/12	89.99	89.00	88.98
	2	+1/80	–1/81	–1/12	92.60	92.35	92.90
	3	–1/40	+1/319	–1/12	71.45	90.33	90.85
	4	+1/80	+1/319	–1/12	68.78	92.30	92.40
	5	–1/40	–1/81	+1/42	85.82	83.70	84.76
	6	+1/80	–1/81	+1/42	92.35	92.70	92.60
	7	–1/40	+1/319	+1/42	90.94	91.17	91.40
	8	+1/80	+1/319	+1/42	93.24	93.80	94.52
Star points	9	–1.682/26	0/200	0/27	82.13	83.03	82.70
	10	+1.682/94	0/200	0/27	87.89	89.68	89.48
	11	0/60	–1.682/0	0/27	90.86	92.60	92.49
	12	0/60	+1.682/400	0/27	91.96	92.70	93.47
	13	0/60	0/200	–1.682/2	92.26	92.93	93.60
	14	0/60	0/200	+1.682/52	88.80	90.85	90.90
Design center	15	0/60	0/200	0/27	89.50	89.40	90.10
	16	0/60	0/200	0/27	89.30	89.10	89.60
	17	0/60	0/200	0/27	89.20	89.70	90.40
	18	0/60	0/200	0/27	88.90	89.00	89.60
	19	0/60	0/200	0/27	90.30	90.80	90.10
	20	0/60	0/200	0/27	88.90	89.40	88.87

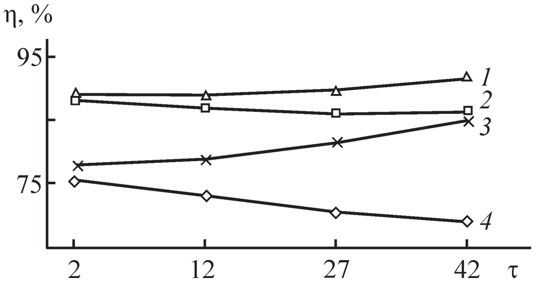

Fig. 6. Kinetic curves of the recovery of organic compounds η from black liquor at different amounts of sulfuric acid taken. (τ) Reaction time; the same for Fig. 7. Sulfuric acid amount, g dm^{-3}: (*1*) 60, (*2*) 40, (*3*) 80, and (*4*) 20.

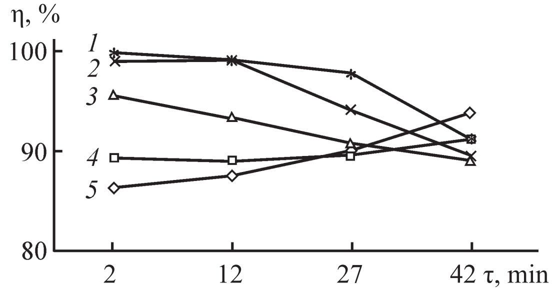

Fig. 7. Kinetic curves of the recovery of organic compounds η from black liquor in the presence of anthraquinone. Anthraquinone concentration, ppm: (*1*) 400, (*2*) 319, (*3*) 200, (*4*) 81, and (*5*) 0.

anthraquinone concentration 400 ppm, and reaction time 2 min.

The reduction of the reaction time to 2 min allows the process flowsheet to be simplified, the use of special reaction equipment to be abandoned, and the reaction to be combined with the filtration.

From the economic standpoint, it is also feasible to perform the process without anthraquinone at the reaction time increased to 42 min.

The continuous process for kraft lignin production by the sulfuric acid procedure [4] has been tested on the semicommercial scale, which considerably reduces risks associated with its mastering.

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