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IMPROVEMENT STUDY FOR THE DEPHENOLIZATION PLANT AT THE RAS "KIVITER" OIL SHALE PROCESSING FACILITY

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A study being conducted to investigate possible improvements in the RAS "Kiviter" dephenolization plant's performance has been carried out. It was found that the streams in the plant fluctuate greatly. The instability with respect to time is partially connected to the cyclical change of the solvent's composition due to hydrolysis reaction. Hydrolysis occurs mainly in the steam stripping column, and, to a lesser extent, in the second distillation column. There is practically no hydrolysis in extraction columns and in the first distillation column. The total rate of the hydrolysis reaction is the lowest when $\text{pH} = 5.55$. Therefore, it is necessary that the pH of incoming water be as close as possible to 5.5, but not excluding this value. In the steam stripping column, it is possible to decrease the decomposition of butyl acetate by applying vacuum to the column. If no direct steam is admitted into the second solvent regeneration column, the amount of phenols in the overhead of the column decreases, and the process of extraction becomes more efficient.

Objectives

This improvement/optimization study for the dephenolization plant at the RAS "Kiviter" oil shale processing facility located in Kohtla-Järve, Estonia, is being conducted to investigate possible improvements in the plant's performance.

The four objectives of the study are as follows:

- To investigate two-stage extraction using butyl acetate and isopropyl ether solvent
- To use a secondary solvent to extract butyl acetate from the water stream
- To investigate applying vacuum to the steam stripping column to reduce steam load and butyl acetate hydrolysis
- To investigate applying vacuum to the second solvent regeneration column to improve separation and product quality

In order to attain an overview of how each stage of process works, authors of this study generated flow sheets for phenols and solvent. An analysis of these flow sheets revealed that in the steam stripping column and, to a lesser degree, in the second solvent regeneration column, hydrolysis of butyl acetate takes place, as a result of which butyl acetate breaks down into butyl alcohol and acetic acid. This is the main reason for the high consumption of solvent. Thus, a special laboratory study was carried out in order to determine the factors influencing the rate of hydrolysis reaction.

Flow Sheets of Phenols and Solvent

Process Description Overview

The dephenolization plant at RAS “Kiviter” serves to remove the mixed phenols from the water stream. After the phenols are removed, the water is sent to the RAS “Kiviter” waste water plant for biological treatment before being discharged into surface water.

The dephenolization plant uses liquid-liquid extraction, steam stripping (butyl acetate removal), and distillation (butyl acetate regeneration) as the unit operations for separating the phenols from the process water as shown in Fig. 1.

Butyl acetate (BA) is currently used as the solvent for removing the phenols from the water stream. The phenol-laden BA is then regenerated and continuously recycled within the plant. The phenols are removed from the solvent and concentrated by distillation.

The dephenolization plant consists of two parallel equipment trains.

Each extraction train consists of four liquid-liquid extraction columns (K1-K4). The columns operate in series with the solvent and water flowing in a counter-current mode. After the water exits the last extraction column, it is fed through heat exchangers to a steam stripping column (K5). The column removes dissolved and emulgated solvent from the water. The cleaned water exits through the bottom of the column and flows through heat exchangers and a storage tank to the waste water treatment plant.

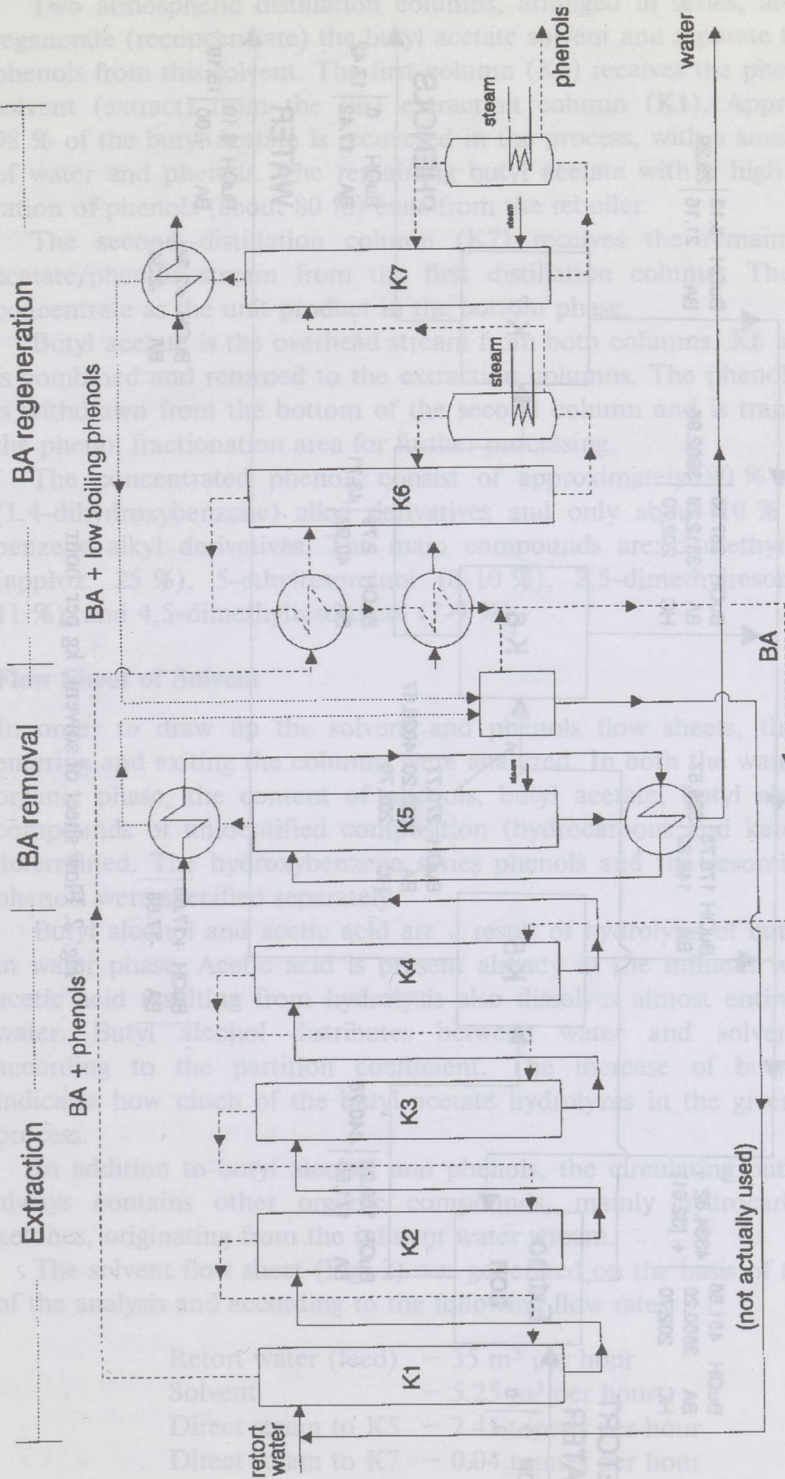


Fig. 1. A simplified flow diagram of the RAS "Kiviter" water dephenolization unit

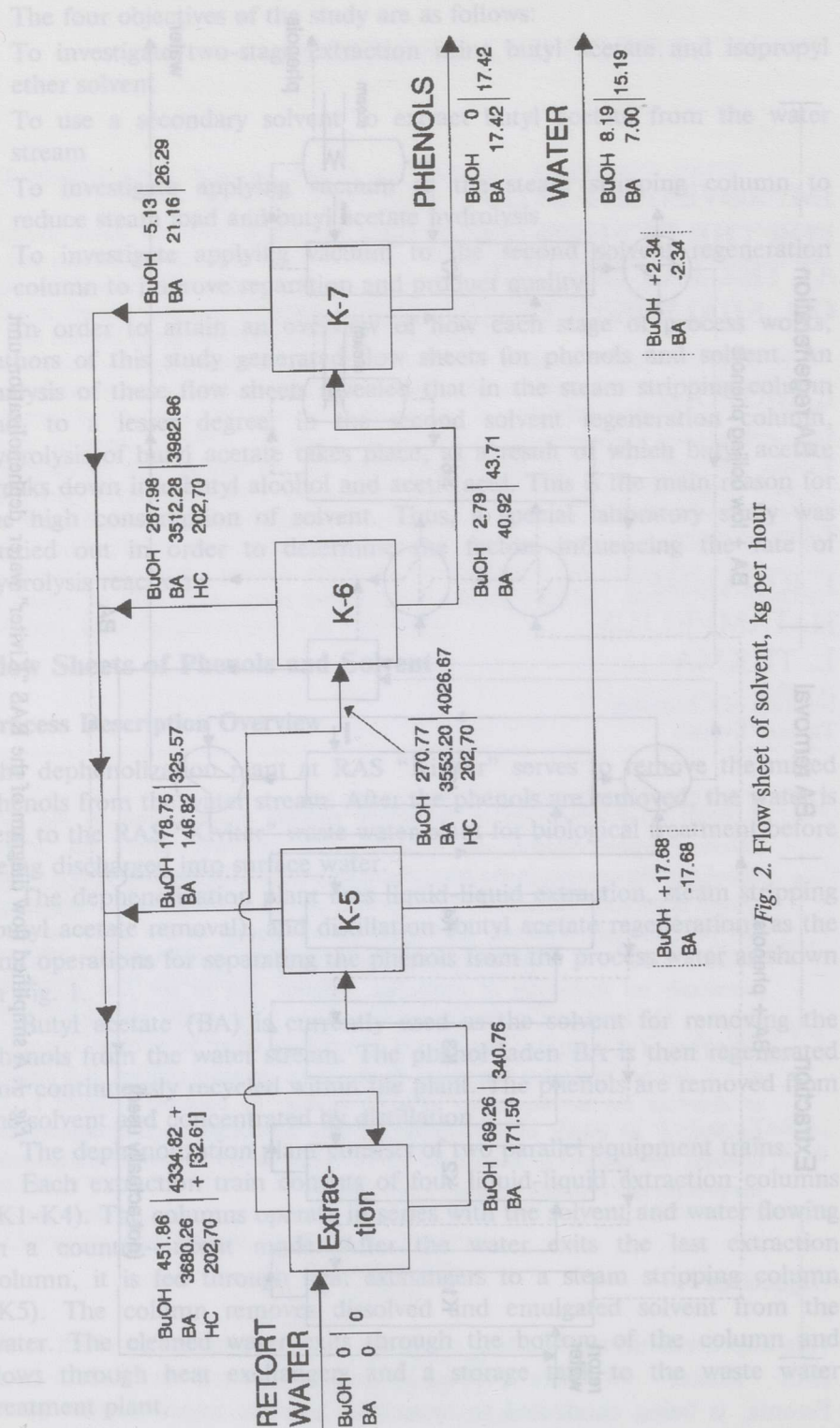


Fig. 2. Flow sheet of solvent, kg per hour

Two atmospheric distillation columns, arranged in series, are used to regenerate (reconcentrate) the butyl acetate solvent and separate the mixed phenols from this solvent. The first column (K6) receives the phenol-laden solvent (extract) from the first extraction column (K1). Approximately 98 % of the butyl acetate is recovered in the process, with a small amount of water and phenols. The remaining butyl acetate with a high concentration of phenols (about 80 %) exits from the reboiler.

The second distillation column (K7) receives the remaining butyl acetate/phenols stream from the first distillation column. The phenols concentrate as the unit product in the bottom phase.

Butyl acetate is the overhead stream from both columns, K6 and K7. It is combined and returned to the extraction columns. The phenols product is withdrawn from the bottom of the second column and is transferred to the phenol fractionation area for further processing.

The concentrated phenols consist of approximately 90 % resorcinol (1,4-dihydroxybenzene) alkyl derivatives and only about 10 % hydroxybenzene alkyl derivatives. The main compounds are: 5-methylresorcinol (approx. 25 %), 5-ethylresorcinol (8-10 %), 2,5-dimethylresorcinol (9-11 %), and 4,5-dimethylresorcinol (7-9 %).

Flow Sheet of Solvent

In order to draw up the solvent and phenols flow sheets, the streams entering and exiting the columns were analyzed. In both the water and the organic phase, the content of phenols, butyl acetate, butyl alcohol and compounds of unidentified composition (hydrocarbons and ketones) was determined. The hydroxybenzene series phenols and the resorcinol series phenols were specified separately.

Butyl alcohol and acetic acid are a result of hydrolysis of butyl acetate in water phase. Acetic acid is present already in the influent water. The acetic acid resulting from hydrolysis also dissolves almost entirely in the water. Butyl alcohol distributes between water and solvent phases according to the partition coefficient. The increase of butyl alcohol indicates how much of the butyl acetate hydrolyzes in the given stage of process.

In addition to butyl alcohol and phenols, the circulating butyl acetate always contains other organic compounds, mainly hydrocarbons and ketones, originating from the influent water stream.

The solvent flow sheet (Fig. 2) was generated on the basis of the results of the analysis and according to the following flow rates:

Retort water (feed)	– 35 m ³ per hour
Solvent	– 5.25 m ³ per hour
Direct steam to K5	– 2.45 tonnes per hour
Direct steam to K7	– 0.04 tonnes per hour

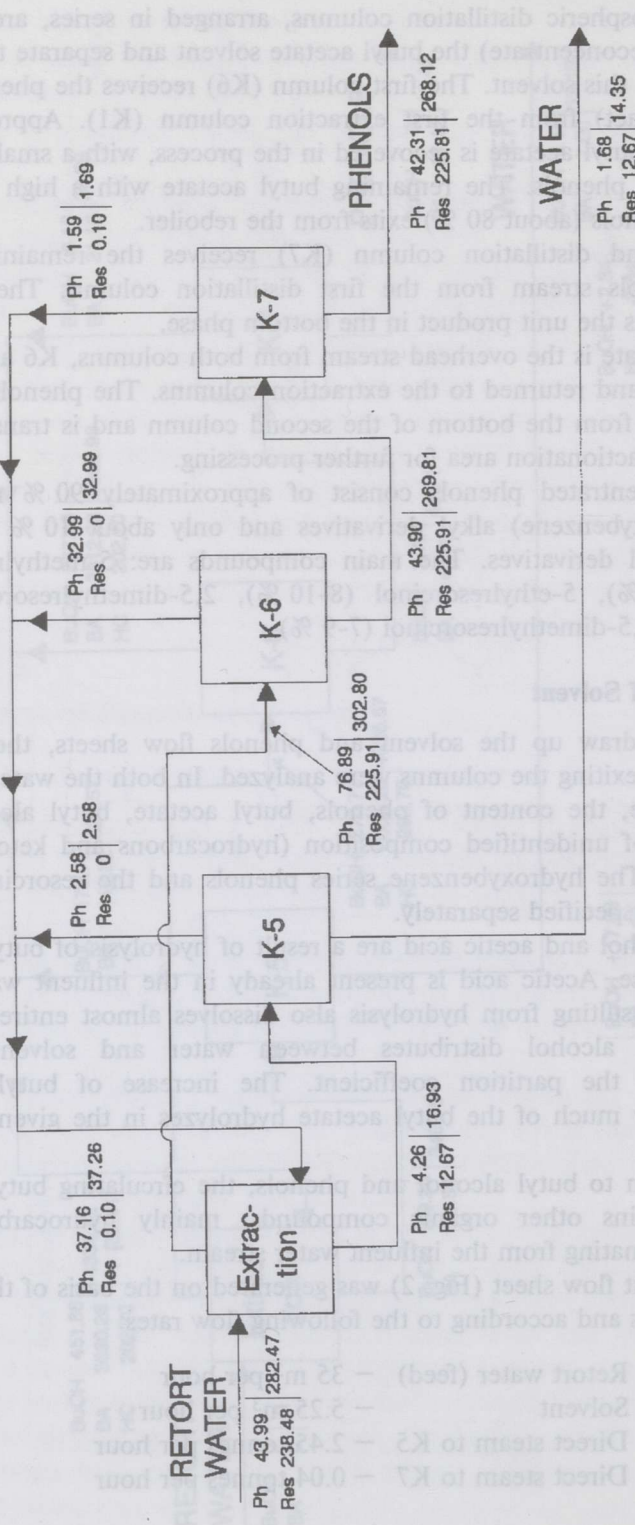


Fig. 3. Flow sheet of phenols, kg per hour

Figure 2 contains the following abbreviations:

Butyl alcohol	–	BuOH
Butyl acetate	–	BA
Hydrocarbons and ketones	–	HC

The number after each vertical dividing-line indicates the total amount of BuOH, BA and HC. The amount of butyl alcohol is given as butyl acetate from which the butyl alcohol originates. One kilogram of butyl acetate corresponds to 0.638 kg of butyl alcohol.

Nevertheless, it must be emphasized that the composition of the samples taken from the streams at different times varies greatly.

Flow Sheet of Phenols

The flow sheet of phenols is depicted in Fig. 3. For this flow sheet, the initial data regarding flow rates are the same as the ones used for the solvent flow sheet.

Figure 3 contains the following abbreviations:

Hydroxybenzene series phenols	–	Ph
Resorcinol series phenols	–	Res

The number after each vertical dividing-line indicates the total amount of Ph and Res.

Discussion

Temporally, the streams in the dephenolization unit fluctuate greatly. The instability with respect to time is partially connected to the cyclical change of the solvent's composition due to hydrolysis. The on-line analyzers of the dephenolization unit do not immediately provide a clear picture of the process' parameters and the unit's operation efficiency. The existent process control system provides only limited opportunities to optimize process parameters.

Presently, in the case of the amount of water to be dephenolized and the solvent to be used, the existing extraction columns without packing allow for a sufficient purification level (phenol content in effluent water at 0.3-0.4 kg per cubic meter) also with respect to the solvent and water ratio of 12 : 100 - 15 : 100 if:

- The amount and composition of streams entering the extraction columns are temporally stabilized.
- The phenol content in the regenerated butyl acetate is kept at a significantly lower level than it is currently.
- The solvent/water phase interface's level in the extraction columns is temporally stabilized.

It is expedient to desist from directing the total overhead from the columns K5, K6 and K7 into the last extraction column (K4). The water

should be separated from the overheads of these columns, either from each stream separately or from the overheads of K6 and K7 together and from the overhead of K5 separately. Consequently, the separated phases should be directed as follows: (1) the water phase from all columns to incoming water as shown in Fig. 1; (2) the organic phase (solvent) from the overhead of column K6 to extraction column K4; (3) the organic phase from the overhead of columns K5 and K7 either to additional rectification or to one of the intermediate extraction columns.

In order to decrease phenol content in the overhead of column K6 (regenerated butyl acetate), (1) reflux to the head of the column should be increased, and (2) the temperature of the reboiler should be decreased, thus, compared to the present, increasing butyl acetate content in the bottom product.

The loss of butyl acetate as a result of hydrolysis reaction is very great. Hydrolysis occurs mainly in column K5 and, to a lesser extent, in column K7. There is practically no hydrolysis in extraction columns and in column K6.

Supplementary studies need to be made in order to discover ways of decreasing hydrolysis.

Two-Stage Extraction Using Butyl Acetate and Isopropyl Ether Solvent

The obtaining and processing of oil-shale phenols (alkyl derivatives of resorcinol) involves the following steps: (1) extraction of phenols from the water stream at the dephenolization plant as shown in Fig. 1; (2) batch rectification of the concentrated phenols obtained to narrow fractions; (3) separation of the crystalline technical-grade 5-methylresorcinol (5-MR) from the fraction enriched in this compound; (4) synthesis of chemical products from crystals and narrow fractions.

Presently, however, steps (2), (3) and (4) are used only periodically, since demand for products manufactured from alkyl derivatives of resorcinol is not great enough.

The process is far from being perfect. In the batch vacuum rectification, the mixed phenols are subjected to a long high-temperature treatment. The resulting condensation of phenols leads to a significant loss of resorcinol derivatives. The batch rectification itself is characterized by a high energy consumption.

The application of another technology for processing oil-shale phenols is considered in the paper [1] published by L. Mölder and H. Tamvelius.

This process consists of the use of two-stage treatment of the incoming water, both stages having independent extractant cycles. In the first stage, the bulk of long-chain resorcinol derivatives and monohydric phenols (hydroxybenzene derivatives) is extracted from the water. In the second

stage, the water is subjected to exhaustive dephenolization. An extract with a high mass fraction of 5-MR is obtained which may be used as a raw material for producing the technical-grade 5-MR.

Putting the two-stage process into practice is possible only if two water dephenolization units exist. Currently, this condition has been fulfilled at RAS "Kiviter".

Nevertheless, the authors of this study have come to the conclusion that use of the two-stage extraction process is not beneficial at this time for the following reasons:

- The process requires isopropyl ether as one of the extractants, which is very expensive to purchase. It is no longer possible to obtain inexpensive by-products of synthesis of isopropyl alcohol from which RAS "Kiviter" would itself extract a narrow cut of isopropyl ether
- The market for technical-grade 5-methylresorcinol is not sufficient

Therefore, only the main results of the authors' earlier studies will be described further.

These results indicate that optimal process conditions are those in which the extractant used in the first stage consists of approximately 67 vol. % butyl acetate and approximately 33 vol. % isopropyl ether. The yield of the end product (concentrated phenols of stage 2) and the concentration of 5-MR in the end product is considerably dependent on the mass fraction of 5-MR in the phenols of the feed stream, which is deduced from the following data:

Mass fraction of 5-MR in the phenols of the feed stream	Mass fraction of 5-MR in the end product	End product, kg per cubic meter of feed stream
0.25	0.62-0.66	0.7-1.1
0.30	0.66-0.70	1.0-1.4
0.35	0.70-0.74	1.2-1.6
0.40	0.74-0.77	1.5-1.9

The results obtained demonstrate that the two-stage process allows the plant to produce concentrated phenols of stage 2 containing 70 % or more of 5-MR. However, the testing of the process of obtaining standard-grade 5-MR from concentrated phenols of stage 2 is necessary.

Use of a Secondary Solvent to Extract Butyl Acetate from the Water Stream

Overview

Presently, in the steam stripping column (K5) dissolved butyl acetate is removed from the water which exits the bottom of the last extraction

column (K4). In order to keep the level of butyl acetate in the water stream which is directed from the dephenolization plant to the biological treatment facility as low as possible, a large amount of direct steam (50-80 kg, at times up to 100 kg per cubic meter of water) must be supplied to the steam stripping column.

In addition, as is confirmed by the flow sheet of solvent (see Fig. 2), the hydrolysis reaction of butyl acetate occurs in the steam stripping column. Therefore, the loss of butyl acetate in the dephenolization plant is considerable, even when the amount of butyl acetate remaining in dephenolized water is small.

The following investigation aims to ascertain whether an alternative method can be applied for removing dissolved butyl acetate from dephenolized water. This method would require less heat (steam) and would not induce intensive hydrolysis of butyl acetate as is presently the case in the steam stripping column.

The idea behind the alternative method is to extract butyl acetate from water using a secondary solvent which does not hydrolyze and which has low solubility in water. Thus, less butyl acetate enters the steam stripping column and, as a result, less steam is required for its stripping. It is also obvious that the lesser the amount of butyl acetate exposed to high temperatures in the steam stripping column, the smaller the amount of butyl acetate broken down through hydrolysis.

Butyl acetate must be regenerated from the extract which is obtained through use of secondary solvent. This can be carried out either in an additional distillation column or, by combining in column K6 the regeneration of both the secondary solvent and the butyl acetate, taking the secondary solvent as the overhead and the butyl acetate as a sidestream.

Partition Coefficients of Butyl Acetate between Hydrocarbon Solvents and Water

In order to choose the most suitable solvent, the partition coefficients between a hydrocarbon solvent and water were experimentally determined. Tests were carried out at a temperature of 20 °C, and the concentration of butyl acetate in the organic phase varied between 1 kg/m³ and 100 kg/m³. The distribution curve was approximated as a straight line.

Since the partition coefficient varies with change in temperature and the actual distribution curve is not exactly a straight line, the attained partition coefficient must be considered approximate and, thus, the results of calculations attained using values of these coefficients should be taken as a rough appreciation.

In Table 1, the values of experimentally determined partition coefficients are calculated as follows:

$$\text{Partition coefficient} = \frac{\text{Concentration of BA in the hydrocarbon phase}}{\text{Concentration of BA in the water phase}}$$

The results shown in Table 1 verify that the most suitable extractants for butyl acetate are aromatic hydrocarbons, especially benzene.

Table 1. Partition Coefficients of Butyl Acetate between Hydrocarbon Solvents and Water at 20 °C, kg m⁻³/kg m⁻³

Solvent	Partition coefficient	Solvent	Partition coefficient
Pentane	51.3	Benzene	236.3
Hexane	48.6	Toluene	163.6
Heptane	46.4	<i>o</i> -Xylene	135.5
Octane	45.0	<i>m</i> -Xylene	124.7
Cyclohexane	55.6	<i>p</i> -Xylene	136.6

RAS "Kiviter" produces benzene and toluene at its pyrolysis plant. For this reason, only these two aromatic hydrocarbons were further studied as possible secondary solvents so as not to necessitate purchase of a secondary solvent from elsewhere.

Solubility of Benzene and Toluene in Water

The secondary solvent's efficiency in extracting butyl acetate from dephenolized water depends, to a great extent, on the solubility of the solvent itself in water and on how much organic phase remains in the water in emulgated form.

Table 2. Solubility of Benzene and Toluene in Water, % by Weight

Temperature, °C	Benzene	Toluene
10	0.158	0.031
20	0.175	0.044
30	0.193	0.061
40	0.211	0.083
50	0.230	0.111
60	0.248	0.145
70	0.268	0.183

Data from various publications were used to calculate the temperature dependence of the solubility of benzene and toluene. Upon comparing the data published by several authors, it was verified that the temperature dependence of solubility can be calculated with great accuracy using the following formula:

$$\ln s = a + b/(t + 273.2) \quad (1)$$

where s is solubility, % by weight; t - temperature, °C; a and b - constants.
 For benzene: $a = 1.17370$, $b = -854.442$.
 For toluene: $a = 6.70754$, $b = 2879.52$.

Solubility in the temperature range of 10-70 °C is as shown in Table 2.

Extraction with Make-Up Benzene and Toluene

The results of one-stage extraction using make-up benzene and toluene depending on the amount of emulgated extract are revealed in Table 3.

Table 3. Results of Extraction Using Make-Up Benzene and Toluene at 20 °C

Extract emulgated, m ³ per 100 m ³ of water	Volume ratio solvent : water	% of BA extracted with	
		benzene	toluene
0	1 : 10	95.9	94.2
	1 : 20	92.2	89.1
	1 : 40	85.5	80.3
0.5	1 : 10	91.1	89.5
	1 : 20	83.0	80.2
	1 : 40	68.4	64.3
1.0	1 : 10	86.3	84.8
	1 : 20	73.8	71.3
	1 : 40	51.3	46.2
1.5	1 : 10	81.5	80.1
	1 : 20	64.5	62.4
	1 : 40	34.2	32.1
2.0	1 : 10	76.7	75.4
	1 : 20	55.3	53.5
	1 : 40	17.1	16.1

The solvent : water volume ratio in the Table 3 represents the solvent : water ratio after the influent water is saturated with solvent. The percentage of BA extracted is defined as:

$$\% \text{ of BA extracted} = \frac{(\text{BA in incoming water} - \text{BA in extracted water}) \cdot 100}{\text{BA in incoming water}}$$

The results presented in Table 3 indicate that the efficiency of extraction using a secondary solvent depends essentially on how much extract remains in the water in emulgated form.

Extraction Using Regenerated Benzene

If a secondary solvent is used at the water dephenolization plant, the solvent must be regenerated (reconcentrated) from the secondary extract

by rectification, either separately in an additional column, or in the existing column K6, withdrawing secondary solvent as the column overhead and butyl acetate as a sidestream. In doing so, it is inevitable that the regenerated secondary solvent always contains, to a certain extent, butyl acetate.

Table 4. Extraction of Butyl Acetate with Regenerated Benzene

BA in incoming regenerated benzene, kg/m ³	Volume ratio benzene : water	No. of counter-current stages	BA in extracted water, g/m ³	% of BA extracted
0	1 : 10	1	159	95.9
		2	8	99.8
	1 : 20	1	302	92.2
		2	12	99.3
	1 : 40	1	561	85.5
		2	93	97.6
20	1 : 10	1	240	93.8
		2	93	97.6
	1 : 20	1	379	90.2
		2	97	97.5
	1 : 40	1	635	83.6
		2	174	95.5
50	1 : 10	1	360	90.7
		2	217	94.4
	1 : 20	1	495	87.2
		2	236	93.9
	1 : 40	1	743	80.8
		2	298	92.3
100	1 : 10	1	565	85.4
		2	430	88.9
	1 : 20	1	693	82.1
		2	449	88.4
	1 : 40	1	921	76.2
		2	507	86.9

Since the difference between the boiling points of butyl acetate (126.5 °C) and toluene (110.6 °C) is much smaller than that of butyl acetate and benzene (80.1 °C), the preferential secondary solvent is then benzene which is less costly to reconcentrate from butyl acetate. In addition, technical-grade butyl acetate always contains a noticeable amount of isobutyl acetate and sec-butyl acetate, the boiling points of which (116.5 °C and 112 °C respectively) do not differ greatly from the boiling point of toluene.

Therefore, only benzene was further studied as a secondary solvent.

The effect of butyl acetate content in incoming regenerated benzene on extraction efficiency was studied. Table 4 provides results of extraction for cases when the butyl acetate content in influent water is equal to its solubility, i.e. 3.87 kg/m^3 , and the effluent water contains no emulgated extract and/or incoming solvent.

Table 5 provides results of extraction when effluent water stream contains 0.5 m^3 of emulgated solvent per 100 m^3 of water.

Table 5. Extraction of Butyl Acetate with Regenerated Benzene
Solvent Emulgated: 0.5 m^3 per 100 m^3 of Water

BA in incoming regenerated benzene, kg/m^3	Volume ratio benzene : water	No. of counter-current stages	BA in extracted water, g/m^3	% of BA extracted
20	1 : 10	1	340	91.2
		2	193	95.0
	1 : 20	1	479	87.6
		2	197	94.9
	1 : 40	1	735	81.0
		2	274	92.9
50	1 : 10	1	610	84.2
		2	343	91.1
	1 : 20	1	745	80.7
		2	486	87.4
	1 : 40	1	993	74.3
		2	548	85.8
100	1 : 10	1	1065	72.4
		2	930	76.0
	1 : 20	1	1193	69.2
		2	949	75.5
	1 : 40	1	1421	63.3
		2	1007	74.0

Conclusions

The most suitable secondary solvent for extraction of butyl acetate from dephenolized water is benzene: (1) it has good ability to extract butyl acetate from water; (2) its solubility in water is low enough; (3) its boiling point is low enough to regenerate it from butyl acetate extract by rectification; (4) it is chemically and thermally stable; (5) it is a product manufactured by RAS "Kiviter".

The efficiency of extraction with a secondary solvent depends largely on (1) how much secondary extract (solvent, when counter-current extraction is used) remains in the water, and (2) how much butyl acetate the regenerated solvent contains. If the separation of phases after extraction is

poor and/or the regenerated solvent contains a large amount of butyl acetate, use of a secondary solvent extraction is ineffective.

Applying Vacuum to the Steam Stripping Column to Reduce Butyl Acetate Hydrolysis

Overview

Water which exits the bottom of the extraction column K4 always contains butyl acetate. Some of the butyl acetate is dissolved in the water, some is in emulgated form. In order to remove butyl acetate from water, it is fed through heat exchangers to a steam stripping column (K5). The column also removes additional monohydric phenols volatile at steam distillation.

Steam to the distillation column is a combination of high-pressure condensate from the solvent regeneration columns after pressure reduction and flashing, and make-up steam. Currently, the distillate from the steam stripping column is combined with regenerated solvent from columns K6 and K7 and returned to the extraction train.

As verified by the flow sheet of solvent (see Fig. 2), it is in the steam distillation column that the butyl acetate hydrolyzes most intensively. This is one of the main reasons for the high consumption of butyl acetate at the dephenolization plant.

As is known, both base (OH^- ions) and acid (H_3O^+ ions) catalyze hydrolysis reaction of esters. Therefore, the rate of hydrolysis of butyl acetate in water phase depends not only on temperature but also on the pH.

In column K5, water always has an acidic reaction. As a result of hydrolysis, acidity increases (pH decreases) even more since an additional amount of acid forms.

Table 6. Solubility of Butyl Acetate in Water

Temperature, °C	% by weight	Mole per cubic meter
20	0.386	33.2
30	0.408	35.1
40	0.430	37.0
50	0.452	38.9
60	0.474	40.8
70	0.495	42.6
80	0.516	44.4
90	0.536	46.2

In order to determine whether hydrolysis of butyl acetate can be decreased, a series of laboratory experiments was carried out. These included study of rate constants of acidic hydrolysis reaction and

determination of butyl acetate's solubility in water depending upon temperature.

Solubility of Butyl Acetate in Water

Results of laboratory experiments revealed the solubility of butyl acetate in water within the temperature range of 20-90 °C. These values are provided in Table 6.

Regularities of the Hydrolysis Reaction

The study of hydrolysis verified the following.

Hydrolysis reaction is a second-order reaction. The rate of reaction is expressed by the following Equation

$$dy/dt = k [BA][H^+] \cdot 10^3 \quad (2)$$

where dy is the amount of BA hydrolyzed in the unit of time dt (hours), mol/m³;

$[BA]$ is the concentration of butyl acetate in water, mol/m³;

$[H^+] \cdot 10^3$ is the concentration of H⁺ (H₃O⁺) ions, mol/m³ (H⁺ = 10^{-pH});

k is the rate constant of the reaction, m³/(mol · h).

If $[BA]$ and $[H^+]$ remain constant, the integral form of Equation (2) is the following:

$$y = 10^3 \cdot k [BA][H^+] t \quad (3)$$

where y is the amount of BA which hydrolyzes within t hours, mol/m³.

If the solution has little buffering capacity, acetic acid, which is a product of the acidic hydrolysis, accelerates the further reaction.

Table 7. Experimental Values of k^*

Temperature, °C	k^* , h ⁻¹	Number of experiments
21.5*1	0.0295±0.0012	18
40	0.0625±0.0011	12
66	0.559±0.003	24
75	1.033±0.006	24
80	1.400±0.030	12
91.5	3.035±0.112	19

1 Not used for calculation of temperature dependence of k^ .

All experiments were carried out under conditions where, throughout the duration of each experiment, water was saturated with butyl acetate. Under such conditions, the butyl acetate concentration $[BA]$ can be replaced with its solubility at the same temperature $[BA]_s$, and Equation (3) can then be expressed as

$$y = 10^3 \cdot k^* [H^+] t \quad (4)$$

where the apparent rate constant $k^* = k[BA]_s$, h^{-1} .

The experimentally verified values of k^* are provided in Table 7.

When temperature rises, the hydrolysis reaction accelerates. The temperature dependence of apparent rate constant k^* can be expressed by the following Equation:

$$\ln k^* = a + b/(273.2 + t) \quad (5)$$

where t is temperature, $^{\circ}\text{C}$;

a and b – constants.

The constants a and b of Equation (5) were calculated on the basis of the apparent rate constants k^* from Table 7. The constants are the following: $a = 24.7808$; $b = -8621.997$; correlation coefficient $r = 0.997$; standard error of $\ln k^*$ estimate $s = 0.087$.

The calculated k^* values based on these constants within the temperature range of 10–100 $^{\circ}\text{C}$ are provided in Table 8.

Table 8. Calculated Values of k^*

Temperature, $^{\circ}\text{C}$	k^* , h^{-1}	Temperature, $^{\circ}\text{C}$	k^* , h^{-1}
10	0.0035	60	0.334
20	0.0098	70	0.711
30	0.0258	80	1.447
40	0.0641	90	2.834
50	0.1501	100	5.354

Actual rate constants k for acidic hydrolysis as a second-order chemical reaction, which were calculated using Equation (3) and the data of Tables 6 and 8, are provided in the Table 9.

Table 9. Values of k

Temperature, $^{\circ}\text{C}$	$10^3 \cdot k$, $\text{m}^3 \text{mol}^{-1} \text{h}^{-1}$	Temperature, $^{\circ}\text{C}$	$10^3 \cdot k$, $\text{m}^3 \text{mol}^{-1} \text{h}^{-1}$
10	0.111	60	8.20
20	0.295	70	16.68
30	0.736	80	32.60
40	1.730	90	61.41
50	3.857	100	111.8

The Value of pH at which the Total Hydrolysis Reaction Is the Slowest

Hydrolysis reaction is catalyzed not only by acid (H_3O^+ ions) but also by alkali (OH^- ions). It was established that the rate constant of alkaline

hydrolysis, k_{alk} , at 25 °C is approximately 800 times higher than the rate constant of acidic hydrolysis reaction, k_{ac} .

The total hydrolysis reaction is the slowest at the pH value where

$$[H^+]/[OH^-] = k_{alk}/k_{ac}. \quad (6)$$

Proceeding from the fact that in water solution

$$[H^+][OH^-] = 10^{-14}$$

and

$$k_{alk}/k_{ac} = 800,$$

it can easily be deduced that the total rate of hydrolysis reaction is the lowest when $[H^+] = 2.83 \cdot 10^{-6}$, i.e.,

$$\text{pH} = 5.55.$$

Therefore, it is necessary that the pH value of the influent water be as close as possible to 5.5, although, it should never be greater than this value. Otherwise, alkaline hydrolysis reaction begins to dominate and, thus, butyl acetate breaks down very rapidly.

At the pH value of 6.5, hydrolysis reaction occurs approximately five times quicker, and at the pH value of 7.5 approximately 50 times quicker than in water which has a pH value of 5.5.

This fact also justifies the deduction arrived at using the flow sheet of solvent, that butyl acetate hydrolysis occurs especially in columns K5 and K7 into which "neutral" direct steam is admitted.

Conclusions

Solubility of butyl acetate in water increases when temperature rises. Nevertheless, solubility's dependence on temperature is not great. In approximate calculations, solubility can be taken as 4 kg per cubic meter.

Hydrolysis of butyl acetate in water occurs as a second-order chemical reaction, the rate of which depends both on the concentration of butyl acetate and the pH of the water solution.

With the decrease of pH by one unit, the acidic hydrolysis reaction accelerates by 10 times and the alkaline hydrolysis reaction slows down by 10 times.

The total rate of hydrolysis reaction is the lowest when $\text{pH} = 5.55$. Therefore, it is necessary that the pH of incoming water be as close as possible to 5.5, but not exceeding this value.

Acidic hydrolysis reaction of butyl acetate accelerates when temperature rises. At 100 °C, the rate of hydrolysis reaction is approximately 1000 times higher than at 10 °C.

In steam stripping column K5, it is possible to decrease substantially the decomposition of butyl acetate due to hydrolysis reaction, by lowering

the temperature by applying vacuum to the column. If, applying vacuum, temperature is decreased by 20 °C, the hydrolysis reaction becomes approximately 4 times slower. To bring the temperature in the steam stripping column to 80 °C, the column should operate at a residual pressure of approximately 0.45 bar (355 mm Hg).

Applying Vacuum to the Second Solvent Regeneration Column

Overview

The second solvent regeneration column (K7) receives the butyl acetate/phenols stream from the first regeneration column. Facility steam is fed to a reboiler to supply the heat for distillation. Steam is also admitted directly to the column to supply additional energy and reduce the distillation temperature.

As can be deduced from the flow sheet of solvent (see Fig. 2), hydrolysis reaction of butyl acetate occurs in the second solvent regeneration column, as does in the steam stripping column (K5), while hydrolysis reaction does not take place in the first solvent regeneration column.

At the same time, the overhead of the second solvent regeneration column sometimes is comprised of up to 30-40 % monohydric phenols volatile with steam. This increases the amount of phenols in the regenerated solvent when overheads from columns K6 and K7 are combined, and decreases the efficiency of extraction.

In order to discover ways to reduce hydrolysis reaction in the second regeneration column, and to improve performance of the column, hydrolysis reaction of butyl acetate in organic phase was studied. It was also determined how phenol content in the regenerated solvent affects phenol content in water after extraction.

Hydrolysis of Butyl Acetate in the Organic Phase

Upon heating up butyl acetate saturated by water, no formation of butyl alcohol and/or acetic acid was found. Hydrolysis reaction was not noticed even when initially butyl acetate contained acetic acid.

Therefore, hydrolysis of butyl acetate in organic phase can be regarded as insignificantly slow, and the main reason for hydrolysis reaction in the second solvent regeneration column is the admission of direct steam into the column.

This conclusion explains the reason for no hydrolysis reaction detected in the first solvent regeneration column.

Table 10. Results of Extraction of Phenols from the Water Stream with Butyl Acetate Containing Hydroxybenzene

α	n	C_W , kg/m ³	Ph%	R%	5-MR%
$C_{SO} = 0$					
0.08	1	2.59	4.8	9.9	53.6
	2	1.37	2.8	16.1	60.3
	3	0.94	1.3	21.7	61.9
	4	0.74	0.6	26.3	61.4
	5	0.63	0.2	29.8	60.0
0.12	1	2.14	4.3	11.0	54.4
	2	1.02	1.9	18.9	60.2
	3	0.66	0.6	25.9	60.1
	4	0.51	0.2	31.5	58.0
	5	0.42	0.1	35.7	55.5
0.16	1	1.86	3.8	11.8	54.9
	2	0.83	1.4	20.9	59.7
	3	0.52	0.4	29.0	58.3
	4	0.39	0.1	35.3	55.0
	5	0.32	—	40.0	51.8
$C_{SO} = 2$					
0.08	1	2.63	6.3	9.7	52.8
	2	1.42	6.2	15.6	58.2
	3	0.99	6.5	20.6	58.7
	4	0.79	7.2	24.5	57.3
	5	0.68	8.0	27.5	55.3
0.12	1	2.18	6.2	10.7	53.4
	2	1.07	6.6	18.0	57.3
	3	0.72	8.0	24.0	55.7
	4	0.56	9.7	28.5	52.4
	5	0.48	11.3	31.7	49.3
0.16	1	1.91	6.2	11.5	53.6
	2	0.88	7.3	19.7	56.2
	3	0.57	9.7	26.3	52.8
	4	0.44	12.2	31.0	48.4
	5	0.37	14.4	34.3	44.4
$C_{SO} = 4$					
0.08	1	2.67	7.7	9.6	52.0
	2	1.47	9.3	15.1	56.2
	3	1.05	11.2	19.6	55.8
	4	0.85	13.0	23.0	53.7
	5	0.74	14.7	25.5	51.3
0.12	1	2.23	8.0	10.5	52.3
	2	1.13	10.9	17.2	54.7
	3	0.77	14.3	22.3	51.8
	4	0.61	17.6	26.0	47.9
	5	0.53	20.3	28.5	44.3
0.16	1	1.95	8.4	11.2	52.3
	2	0.93	12.5	18.6	53.0
	3	0.62	17.4	24.1	48.3
	4	0.49	21.7	27.6	43.1
	5	0.43	25.1	30.0	38.8

The Effect of Phenols Contained in Regenerated Solvent on the Extraction

Division of monohydric phenols between the overheads of columns K6 and K7, such as the one shown in the flow sheet of phenols, is rather irregular than typical. Usually, monohydric phenols (hydroxybenzene alkyl derivatives) go into the regenerated solvent with the overhead of the second solvent regeneration column. If concentration of phenols in the overhead of the second solvent regeneration column can be successfully reduced by replacing direct steam with vacuum, the concentration of phenols in the effluent water decreases also.

Table 10 provides the concentration of phenols in effluent water when extracted by counter-current mode. These are arrived at assuming that:

- Concentration of phenols in influent water is 11.0 kg/m^3
- Composition of phenols is the following, % by weight:

Hydroxybenzene derivatives	– 10.8 %
Among them hydroxybenzene	– 4.5 %
Resorcinol	– 3.2 %
2-Methylresorcinol	– 1.8 %
4-Methylresorcinol	– 1.9 %
5-Methylresorcinol	– 29.8 %
2,5-Dimethylresorcinol	– 10.6 %
5-Ethylresorcinol	– 10.2 %
4,5-Dimethylresorcinol	– 9.2 %
2-Methyl-5-ethylresorcinol	– 5.1 %
Other resorcinol derivatives	– 17.4 %
- The distribution curves of phenols can be approximated as published in [2-4]
- Extraction temperature $20 \text{ }^\circ\text{C}$

Abbreviations and notations used in Table 10 are the following:

α - volume ratio butyl acetate : water;

n - number of theoretical stages;

C_W - concentration of phenols in the effluent water stream, kg/m^3 ;

C_{SO} - concentration of hydroxybenzene in regenerated (influent) solvent, kg/m^3 ;

$Ph\%$, $R\%$, $5-MR\%$ - % by weight of hydroxybenzene, resorcinol and 5-methylresorcinol, respectively, in the mixed phenols which remain unextracted.

Conclusions

In organic phase, butyl acetate does not hydrolyze practically at all. Hydrolysis of butyl acetate in the second solvent regeneration column is caused only by direct steam fed into the column. If direct steam is replaced by vacuum, hydrolysis reaction no longer occurs in the column.

If no direct steam is admitted into the second solvent regeneration column, the amount of phenols volatile with steam in the overhead of that column decreases, and the process of extraction of phenols from the water stream becomes more efficient.

Whether employment of vacuum also improves the quality of the product (concentrated phenols) by decreasing the condensation and polymerization of phenols, can be determined only upon actual experiments at the water dephenolization plant.

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