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TWO-STAGE EXTRACTION OF ALKYL RESORCINOLS FROM OIL SHALE TAR WATER

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ДВУХСТАДИЙНАЯ ЭКСТРАКЦИЯ АЛКИЛРЕЗОРЦИНОВ ИЗ СЛАНЦЕВЫХ СМОЛЬНЫХ ВОД

The alkyl derivatives of resorcinol (AR) obtained from the tar (phenolic) water of oil shale processing, are a unique raw material for the chemical industry. This is why their rational utilization is of great importance.

At present, the technology of obtaining and processing oil shale AR (so-called water-soluble phenols) involves the following steps: (1) extraction of phenolic compounds from the averaged tar water, (2) rectification of the extract obtained to narrow fractions, (3) separation of the crystalline technical grade 5-methylresorcinol (5-MR) from the 280—295 °C fraction enriched in this compound, and (4) synthesis of chemical products from these crystals and narrow fractions.

Such a technology is rather far from being perfect; this applies especially to the extraction of AR from tar and other phenol waters with isopropyl ether, butyl acetate or most frequently, their mixture. Rather unwieldy is also another key stage of AR technology, batch vacuum rectification of total water-soluble phenols. In this process the mixture of AR is subjected to long high-temperature treatment. The resulting condensation of phenolic compounds leads to a significant loss of AR. The batch rectification itself is characterized by a high specific energy consumption.

In this paper, the applicability of another system to processing AR will be considered. It consists in two-stage (two-step) treatment of the incoming phenolic water by the mixed extractant (mixture of butyl acetate and isopropyl ether), both the stages having independent extractant cycles. In the first stage the bulk of long-chain AR and monohydric phenols is extracted from the water. In the second stage, the water is subjected to exhaustive dephenolization and an extract with a high mass fraction of 5-MR is obtained. The extract may be used as a raw material for obtaining the technical grade 5-MR.

The idea of using two-stage extraction is not new. It is, hovewer, true that in its initial shape the idea was to obtain the extract free of monohydric phenols, but not the raw concentrate of 5-MR [1, 2].

Putting into practice the two-stage system is possible only if two water dephenolization units with a capacity high enough enabling their series connection are available. At present this condition has been fulfilled at the "Põlevkivikeemia" Production Association at Kohtla-Järve.

Separation of compounds by two-stage extraction

The idea of applying the two-stage system is based on the well-known fact that partial Gibbs excess energies ($\bar{G}^E$) of AR in water (W) and

organic solvent (S) depend considerably on the structure of their molecule. As a rule, the higher the number of carbon atoms in the substituents of the aromatic ring and the nearer the substituents to the hydroxyl groups, the greater the $\bar{G}^E$ of AR in water. But in organic solvents, an increase in the alkylation degree of the resorcinol molecule leads to a decrease in its $\bar{G}^E$. The partition coefficient of the compound i between S and W ($K_{i(S/W)}$) is determined by the condition of equality of its chemical potential in equilibrium phases, i. e. by the difference of $\bar{G}^E$ in W ($\bar{G}^E_{i(W)}$) and S ($\bar{G}^E_{i(S)}$):

$$RT \ln K_{i(S/W)} \equiv RT \ln (x_{i(S)}/x_{i(W)}) = RT \ln (\gamma_{i(W)}/\gamma_{i(S)}) = \bar{G}^E_{i(W)} - \bar{G}^E_{i(S)}, \quad (1)$$

where x — the mole fraction, γ — the thermodynamic activity coefficient.

The lower the number of carbon atoms in the alkyl substituents and the farther the substituents from the OH-groups in the aromatic ring the lower the partition coefficients of the AR. Therefore the extraction of 5-MR and, especially, resorcinol is less exhaustive than that of the other AR present in oil shale tar water.

Taking one of the partitioning component j as a standard, the selectivity of the extractant in relation to component i (β_{ij}) may be expressed as follows:

$$\ln \beta_{ij} \equiv \ln(K_{i(S/W)}/K_{j(S/W)}) = (\bar{G}^E_{i(W)} - \bar{G}^E_{j(W)}) - (\bar{G}^E_{i(S} - \bar{G}^E_{j(S)}). \quad (2)$$

Let j be the less alkylated compound, e.g. 5-MR. Then

$$\bar{G}^E_{i(W)} - \bar{G}^E_{j(W)} > 0, \quad (3)$$

$$\bar{G}^E_{i(S)} - \bar{G}^E_{j(S)} < 0, \quad (4)$$

and

$$\ln \beta_{ij} > 0 \quad (5)$$

i. e. the extraction of compound i with organic solvent is, as a rule, more exhaustive than that of j. However, in case of polar solvents

$$\bar{G}^E_{i(S)} - \bar{G}^E_{j(S)} \approx 0 \quad (6)$$

and the selectivity in relation to long-chain AR is low.

Distribution of AR on countercurrent extraction (Stage I)

To estimate the selectivity in relation to individual compounds in Stage I of the two-stage extraction balances of individual compounds in various extraction conditions were established. The analytical forms of extraction isotherms of the major components of AR published by the authors earlier [3, 4] were used. The total concentration of phenols in the feed (incoming water) C_{W0}, temperature and number of theoretical stages were fixed on a predetermined level (11 kg/m^3, 40 °C and 3, respectively). The ratio of individual components of AR (except 5-MR) in the feed was taken according to the average data of "Põlevkivikeemia" Production Association. The mass fraction of 5-MR in the AR of the incoming water (4 values from 0.25 to 0.40), the volume fraction of butyl acetate in the

extractant (5 values from 0.3 to 1.0) and the residual concentration of AR in water C_{WI} (4 values from 1.2 to 2.5 kg/m^3) were varied.

Using the methods described in [5, 6] the composition of AR in the extract and raffinate phases and the extractant to water ratio, S/W, required to achieve the design C_{WI} at all possible parameter value combinations were determined.

To establish the quantitative relation between the mass fraction of 5-MR in the AR of the raffinate of Stage I (y_I) and process parameters regression analysis of the results obtained (80 values of y_I in all) was carried out. It was found that y_I is adequately (the multiple correlation coefficient $R = 0.987$, standard deviation of the values of y_I $s = 0.0056$) described by the equation:

$$y_I = b_0 + b_1x_1 + b_4x_4 + b_5x_3(1 - x_3) + b_6x_4(1 - x_4), \qquad (7)$$

where x_1 — the mass fraction of 5-MR in the AR of the feed (incoming water), x_2 — the ratio of AR concentration in the raffinate to that in the feed phase, ($x_2 = C_{WI}/C_{W0}$), x_3 — the relative depth of extraction of AR ($x_3 = x_2/x_1$), x_4 — the volume fraction of butyl acetate in the mixed extractant, $b_0 = 0.416 \pm 0.066$, $b_1 = 0.555 \pm 0.012$, $b_4 = 0.037 \pm 0.005$, $b_5 = 0.152 \pm 0.016$, $b_6 = 0.010 \pm 0.012$.

The inclusion of additional terms, b_2x_2 and b_3x_3 in the regression equation will not essentially improve the correlation, while the reliability of regression coefficients is low.

Equation (7) demonstrates, that the 5-MR mass fraction in the AR of the feed (incoming water) influence y_I most. The influence of both the ratio $x_3 = x_2/x_1$ and the composition of extractant x_4 is relatively low. Maximum y_I is observed when $x_3 = 0.50$ and $x_4 = 0.667$ (Figs. 1 and 2).

Data about the extractant — water ratio required z_I ($z_I = S/W$, m^3/m^3) were also subjected to regression analysis. Thus it was established that

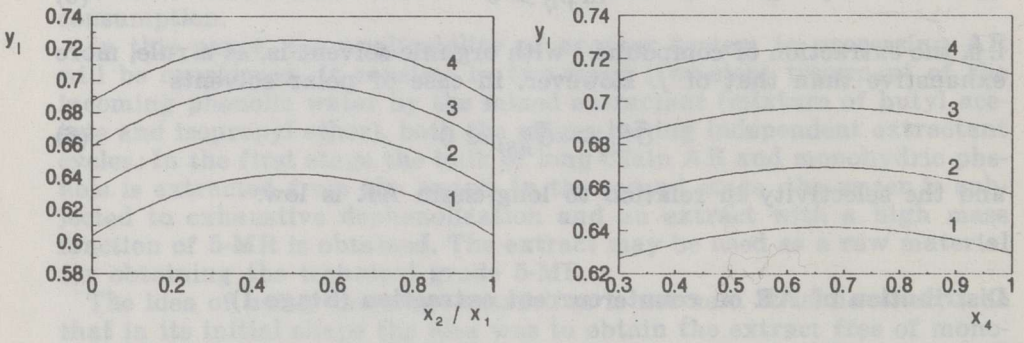

Fig. 1. Mass fraction of 5-MR y_I in the AR of the raffinate of Stage I at $x_4 = 0.667$. Mass fraction of 5-MR in the AR of the feed (x_1): *1* — 0.25, *2* — 0.30, *3* — 0.35, *4* — 0.40

Рис. 1. Доля 5-метилрезорцина y_I в фенолах рафината I стадии при $x_4 = 0{,}667$. Доля 5-метилрезорцина в фенолах исходной воды (x_1): *1* — 0,25, *2* — 0,30, *3* — 0,35, *4* — 0,40

Fig. 2. Mass fraction of 5-MR y_I in the AR of the raffinate of Stage I at $x_2/x_1 = 0.50$. Designations of curves see in Fig. 1

Рис. 2. Доля 5-метилрезорцина y_I в фенолах рафината I стадии при $x_2/x_1 = 0{,}50$. Обозначения кривых см. в подписи к рис. 1.

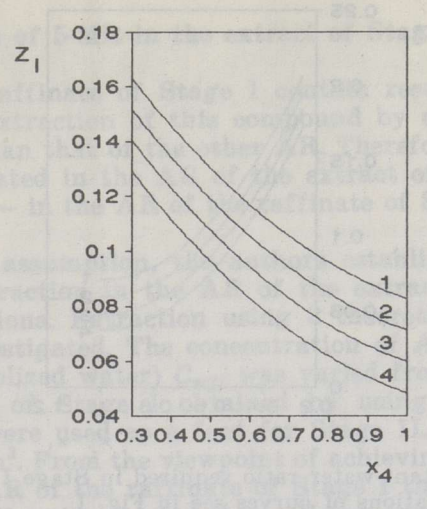

Fig. 3. The extractant-water ratio required in Stage I z_I (m^3/m^3) at $x_2/x_1 = 0.50$. Designations of curves see in Fig. 1

Рис. 3. Расход экстрагента в I стадии z_I ($м^3/м^3$) при $x_2/x_1 = 0.50$. Обозначения кривых см. в подписи к рис. 1

the dependence of z_I on the process parameters can be adequately ($R = 0.968$, $s = 0.0115$) described by the equation

$$z_I = b_0 + b_1x_1 + b_3x_3 + b_4x_4 + b_5x_3(1 - x_3) + b_6x_4(1 - x_4), \qquad (8)$$

where $b_0 = 0.468 \pm 0.019$, $b_1 = -0.227 \pm 0.027$, $b_3 = -0.243 \pm 0.010$, $b_4 = -0.144 \pm 0.009$, $b_5 = -0.252 \pm 0.039$, $b_6 = -0.098 \pm 0.025$.

As in case of equation (7), the inclusion of an additional term, b_2x_2 in equation (8) will not essentially improve the correlation.

z_I is strongly dependent on x_1, x_3 and x_4 (Figs. 3—5).

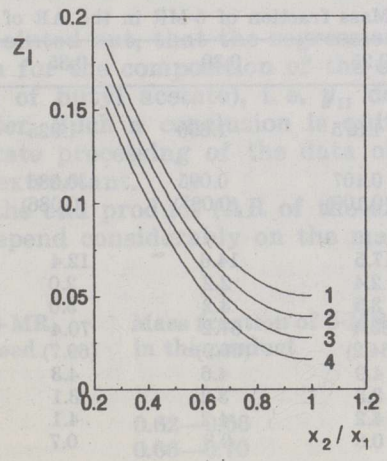

Fig. 4. The extractant-water ratio required in Stage I z_I (m^3/m^3) at $x_4 = 0.50$. Designations of curves see in Fig. 1

Рис. 4. Расход экстрагента в I стадии z_I ($м^3/м^3$) при $x_4 = 0{,}50$. Обозначения кривых см. в подписи к рис. 1

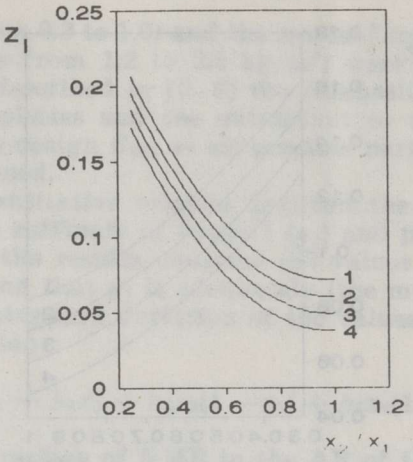

Fig. 5. The extractant-water ratio required in Stage I z_I (m^3/m^3) at $x_4 = 0.667$. Designations of curves see in Fig. 1

Рис. 5. Расход экстрагента в I стадии z_I ($м^3/м^3$) при $x_4 = 0{,}667$. Обозначения кривых см. в подписи к рис. 1

Increasing x_3 and x_4 leads to an appropriate decrease in the extractant — water ratio. When x_3 and x_4 are constant, an increase in x_1 is also accompanied by a decrease in z_I. On the face of it this appropriateness may seem illogical. However, taking into account that increasing x_1, while x_3 is constant, means increasing the residual concentration of AR, and such a relation between x_1 and z_I proves to be quite natural.

Even under optimum conditions of producing the AR of the raffinate with a minimum 5-MR concentration of 70 % the AR of the feed must contain at least 35 % of this compound (Table). The yield of 5-MR (its amount in the raffinate) is 35—37 % of the total amount in the feed.

The extractant-water ratio required and composition of AR of the raffinate of Stage I using 3 theoretical contacts and optimum extraction conditions ($x_2/x_1 = 0.50$, $x_4 = 0.667$)

Расход экстрагента и состав АР рафината I стадии в оптимальных условиях экстракции ($x_2/x_1 = 0{,}50$, $x_4 = 0{,}667$, 3 теоретических ступени)

	Mass fraction of 5-MR in the AR of the feed			
	0.25	0.30	0.35	0.50
AR concentration in the raffinate, kg/m^3	1.375	1.650	1.925	2.200
The extractant-water ratio required, m^3/m^3*	0.107 (0.109)	0.095 (0.097)	0.086 (0.086)	0.079 (0.075)
Composition of AR, %:				
resorcinol	17.5	14.6	12.4	10.6
2-methylresorcinol	2.4	2.2	2.0	1.8
4-methylresorcinol	3.5	3.2	3.0	2.7
5-methylresorcinol**	63.4 (64.2)	67.2 (66.9)	70.4 (69.7)	73.3 (72.5)
2,5-dimethylresorcinol	4.9	4.6	4.3	4.0
5-ethylresorcinol	3.3	3.2	3.1	3.0
4,5-dimethylresorcinol	4.2	4.2	4.1	3.9
2-methyl-5-ethylresorcinol	0.8	0.8	0.7	0.7
Yield of 5-MR in the raffinate, % of total amount in the feed	31.7	33.7	35.2	36.7

* in brackets — according to equation (8).
** in brackets — according to equation (7).

The concentration of 5-MR in the extract of Stage II

The AR of the raffinate of Stage I contain resorcionol as the major admixture. The extraction of this compound by organic extractants is less exhaustive than that of the other AR. Therefore it is supposed that 5-MR is concentrated in the AR of the extract of Stage II (main product), resorcinol — in the AR of the raffinate of Stage II (dephenolized water).

To verify this assumption, the authors established a dependence of the 5-MR mass fraction in the AR of the extract of the Stage II on extraction conditions. Extraction using 3 theoretical stages of contact at 40 °C was investigated. The concentration of AR in the raffinate of Stage II (dephenolized water) C_{WII} was varied from 0.3 to 0.7 kg/m^3.

The raffinates of Stage I obtained by using the extractant with $x_4 = 0.50—0.85$ were used as a feed for Stage II. Their content of AR was 2.0—2.5 kg/m^3. From the viewpoint of achieving a maximum content of 5-MR in the AR of the raffinate of Stage I these conditions are not optimum, but still quite similar them. Using this feed in the Stage II of extraction enables us to increase the yield of the desired product without any substantial deterioration of its quality.

The results obtained demonstrate, that the mass fraction of 5-MR in the AR of Stage II, y_{II}, depends mainly on the mass fraction of this compound in the AR of the raffinate of Stage I ($x_1 \equiv y_I$) used as a feed in Stage II. When the AR concentration in the dephenolized water C_{WII} is varied from 0.3 to 0.7 kg/m^3, the dependence of y_{II} on the ratio the AR concentration in the feed to that in the raffinate X_2 ($X_2 \equiv C_{WII}/C_{WI}$) is quite low.

X_1 is naturally determined by the conditions of extraction in the Stage I, and for Stage II it cannot be chosen at will. Increasing X_1 leads to an increase in y_{II}. Dependence of y_{II} on X_2 or X_2/X_1 has no clearly distinguished maximum. The regression equation adequately describing the whole set of y_{II} values is as follows:

$$y_{II} = -0.077(\pm 0.008) + 1.158(\pm 0.011)X_1 - 0.029(\pm 0.04)X_2/X_1 \quad (9)$$

$$(n = 144,\ R = 0.994,\ s = 0.005).$$

It should be pointed out, that the regression equation for y_{II} does not include the term for the composition of the extractant of Stage II (the volume fraction of butyl acetate), i. e. y_{II} does not practically depend on this parameter. Such a conclusion is quite appropriate and is confirmed by separate processing of the data obtained at any fixed composition of the extractant.

The yield of the end product (AR of the extract of Stage II) and its 5-MR content depend considerably on the mass fraction of 5-MR in the AR of the feed.

Mass fraction of 5-MR in the AR of the feed (incoming water)	Mass fraction of 5-MR in the product	The product yield, kg/m^3 of incoming water
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 extraction allows us in principle to obtain the extract of Stage II containing 5-MR 70 %

and more. However, to evaluate the prospects of the system, the testing of the technology of standard technical grade 5-MR on the basis of this raw product, especially its purification from coloured substances, is necessary.

Conclusions

1. An improved system for dephenolization of Kukersite oil shale tar water has been studied. This consists in the two-stage treatment of the incoming water by the mixed extractant, both the stages having independent cycles of extractant. In the Stage I, the bulk of the monohydric phenols and long-chain resorcinols is extracted from water. In the Stage II water is subjected to exhaustive dephenolization and the resorcinol-series phenols of the extract enriched in 5-methylresorcinol are obtained.
2. A dependence of the extractant — water ratio required to achieve the design residual concentration of AR in water and the mass fraction of 5-MR in the AR of the raffinate of Stage I on the composition of AR in the feed (incoming water), the composition of the mixed extractant and the relative depth of AR extraction has been established.
3. It has been found that in industrial conditions the main product with a 5-MR content of 70 % or more can be obtained.

РЕЗЮМЕ

В статье рассматривается возможность использования усовершенствованной схемы извлечения алкилрезорцинов (АР) из сланцевых смольных (фенольных) вод. Она заключается в двухстадийной обработке исходной фенольной воды смешанным экстрагентом (смесью бутилацетата и диизопропилового эфира), причем обе стадии имеют самостоятельные циклы экстрагента. В первой стадии из воды извлекается основная часть длинноцепочечных АР и одноатомных фенолов. Фенолы, не экстрагированные в первой стадии, обогащаются резорцином и 5-метилрезорцином (5-МР). Во второй стадии проводят исчерпывающую дефеноляцию воды, и получают экстракт с высоким содержанием 5-МР. Этот экстракт намечается использовать как сырье для получения концентрата 5-МР.

Идея использования двухстадийной схемы основывается на известном факте, что парциальные избыточные энергии Гиббса ($\bar{G}^E$) АР в воде (W) и органическом растворителе (S) существенно зависят от строения их молекулы. Чем больше атомов углерода в заместителях ароматического ядра и чем ближе заместители расположены к гидроксильным группам, тем больше $\bar{G}^E$ АР в воде. В органических же растворителях повышение степени алкилирования молекулы резорцина приводит к уменьшению его $\bar{G}^E$. Поэтому 5-МР и, особенно, резорцин экстрагируется хуже остальных АР, содержащихся в сланцевой смольной воде.

Для оценки селективности экстракции в I стадии процесса при различных комбинациях параметров процесса (массовая доля 5-МР в фенолах поступающей воды, объемная доля бутилацетата в экстрагенте, остаточная концентрация фенолов в воде) определяли балансы отдельных соединений и расход экстрагента данного состава, необходимый для достижения заданной остаточной концентрации в воде. При фиксированных суммарной концентрации фенолов в исходной воде, температуре и числе теоретических ступеней контакта (соотвественно 11 кг/м^3, 40 °С и 3 теоретических ступени) массовая доля 5-МР в фенолах рафината I ступени (y_1 удовлетворительно описывается с помощью регрессивного уравнения (7) (x_1 — массовая доля 5-МР в фенолах поступающей воды, x_2 — соотношение остаточной и исходной концентраций фенолов в воде, $x_3 = x_2/x_1$, x_4 — объемная доля бутилацетата в экстрагенте).

На y_I наибольшее влияние имеет x_1. Включение в уравнение (7) дополнительного члена b_2x_2 не приводит к сколько-нибудь существенному улучшению корреляции. Максимум y_I наблюдается при $x_3 = 0{,}50$ и $x_4 = 0{,}667$, но влияние обоих этих параметров относительно невелико (рисунки 1 и 2).

Зависимость относительного расхода экстрагента, необходимого для достижения заданной остаточной концентрации фенолов в воде (z_I, м^3/м^3 воды), от параметров процесса описывается с помощью уравнения (8). z_I существенно зависит от x_1, x_3 и x_4 (рисунки 3—5).

Для получения фенолов рафината с содержанием 5-МР не менее 70 % содержание этого соединения в фенолах исходной воды должно быть как минимум порядка 35 % (таблица). При этом выход 5-МР (количество его в фенолах рафината) составляет 35—37 % от его количества в поступающей воде.

Фенолы экстракта II ступени (целевой продукт) дополнительно обогащаются 5-метилрезорцином, фенолы рафината II стадии (дефенолированной воды) — резорцином. Доля 5-МР в фенолах экстракта II стадии y_{II} зависит в основном от его доли в фенолах рафината I стадии, поступающего в II стадию X_1 ($X_1 = y_I$). Набор величин y_{II} описывается с помощью уравнения (9).

Выход целевого продукта и доля в нем 5-МР существенно зависит от концентрации этого соединения в фенолах исходной воды. В условиях процесса, реальных для осуществления в промышленности, выход целевого продукта можно оценить следующим образом:

Доля 5-МР в фенолах исходной воды	Доля 5-МР в целовом продукте	Выход целевого продукта, кг/м^3 воды
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

Для окончательной оценки перспективности схемы двухстадийной экстракции необходимо испытать технологию получения из этого сырого экстракта II стадии кондиционного 5-МР технической чистоты, особенно очистку его от окрашенных веществ.

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