Industrial application of the hollow fiber modules in the process of extraction of phenol from the hydrocarbon fraction

Tadeusz Porebski¹, Sławomir Tomzik¹, Włodzimierz Ratajczak¹ Marzena Talma-Piwowar¹, Arkadiusz Wieteska², Michał Żebrowski², Miroslaw Karabin²
¹ IChP - Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland
² Polski Koncern Naftowy ORLEN SA. Plock
E-mail: Tadeusz.Porebski@ichp.pl

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Launching of the hollow fiber contactors in the liquid-liquid extraction process of phenol from the hydrocarbon fraction with a 16% by wt. aqueous NaOH is presented. The block scheme of the process is discussed. The extraction process is operated in two stages each applying eight 4” x 28” contactors arranged parallel. The industrial plant capacity is 550-650 kg/h of hydrocarbon fraction containing average 2-4% by wt. of phenol. The plant works with very high efficacy of 98.5-99.5% i.e. the phenol content in the dephenolized product is below 0.02% wt.

INTRODUCTION

Solvent extraction has often been used for separating and/or isolating chemical compounds. The efficiency of the extraction process is closely related to the interface area through which mass is transferred. This interface area is composed of two insoluble phases (organic or aqueous) containing various amounts of the extracted species (solute). In the classical extraction process, dispersing one phase (e.g., in the form of droplets) generates the interface. After the process has been completed, the phases are allowed to separate into the extract and the raffinate. Therefore, differences in density, viscosity, and surface tension between both phases make very important parameters for extraction process realised in conventional equipment including columns, mixers-settlers or centrifuges. In many cases too little density and/or surface tension differences cause formation of stable emulsions that are difficult to break. In the systems of high surface tension value creation of a large interface area for mass transfer is rather difficult and implies use of large-size apparatus.

A new non-dispersive phases contacting technology has been work out. In the process hollow fiber membrane modules are used to generate the interfacial area. The idea of the process is shown schematically (Fig 1) for a hydrophobic fibre membrane.

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**Fig.1.** The idea of the membrane-based solvent extraction
The organic phase flows inside the hollow fibers (in the membrane tube side) and spontaneously wets (fills) membrane pores. To block the flow of organic phase through the membrane pores, another phase (e.g. water) is introduced to the shell side of the hollow fiber module. As indicated in the scheme, a slight overpressure is maintained over the pressure on the organic phase. This overpressure immobilises the interface on the surface of the membrane pores.

The essential advantages of the application of the hollow fiber membrane as extractor apparatus in the liquid-liquid extraction processes comparing with conventional extraction columns are as follows:

- a very favourable ratio of the mass transfer surface area to the apparatus volume - for typical modules this ratio ranges from 4000 to 10.000 m²/m³;
- no phases dispersion - phase separator is not required;
- stream flow rates can be varied within a broad range with no effect on process hydrodynamics (no flooding nor channelling problems),
- easy scaling-up - involves module build-up only.

PKN ORLEN SA. Płock produces phenol and acetone by the cumene method. The process involves production of maximum 650 kg/h of a by-product stream of a phenol-containing hydrocarbon fraction. The hydrocarbon feed - a mixture containing mainly α-methylstyrene (40-45% wt.) and cumene (50-55% wt.) - contains also phenol of the level 2-4 % wt. The fraction used to be fed for the gasoline composition.

A new method of utilisation of the hydrocarbon fraction has been worked out at IChP (Industrial Chemistry Research Institute) in Warsaw. It enables processing of the fraction to a full-value raw material for phenol and acetone synthesis. The key operation of the novel process is extractive removal of phenol from the stream with aqueous soda lye. In the process of phenol extraction membrane contactors are used as extractor.

**EXPERIMENTAL (pilot plant study)**

Results of the pilot-plant study carried out at the Phenol and Acetone Plant of the PKN ORLEN Company, Płock are presented below. A pilot plant set-up with the Hoechst Celanese Liqui-Cel Extra Flow Contractor 4” x 28” in size was used as membrane extractor. Module parameters and fiber characteristics are presented in Table 1. The module contains polypropylene microporous hydrophobic Celgard® X-40 hollow fibres.

| Table 1. The characteristics of the Liqui-Cel Extra Flow Contactor 4” x 28” |
|---------------------------------|------------------|
| **Membrane parameters**        |                  |
| Type                            | hollow-fiber, CELGARD X-40 |
| Material                        | hydrophobic polypropylene |
| Internal diameter, µm           | 240               |
| Wall thickness, µm              | 30                |
| Pore diameter, µm               | 0.03              |
| Porosity, %                     | 40                |
| Effective fiber length, cm      | 60.0              |
| **Module parameters**           |                  |
| Internal diameter, cm           | 10.0              |
| Total number of fibers          | 42000             |
| Surface area/volume ratio, cm²/cm³ | 36.0            |
| Packing density                 | 0.35              |
| Contact surface area, m²        | 19                |
The same membrane modules as described in the Table 1 were applied in the full-scale extraction process.

A countercurrent stream flowsheet is presented in Fig. 2. In each experiment, the feed (phenol-containing hydrocarbon fraction) was introduced to the tube side of the membrane module. The flow rate of the organic phase varied from 50 L/h to 100 L/h. In the all pilot plant tests, there was no recycling of the technological streams through the membrane contactors.

![Diagram of pilot plant installation](image)

**Fig. 2.** Scheme of the pilot plant installation.

The pilot-plant study was to determine process parameters for the modules operating in the full-scale conditions. Fig. 3 shows the influence of change in hydrocarbon fraction feed on the degree of dephenolization of the treated fraction. The hydrocarbon fraction feed used on the pilot plant tests contained about 3.0 % wt. of phenol. Phenol concentrations in organic phase and in the aqueous phase were determined by gas chromatography and by UV spectrophotometric analysis.

![Graph showing efficiency of dephenolization](image)

**Fig. 3.** The efficiency of phenol extraction in relation to hydrocarbon fraction flow – pilot plant study.

Amount of aqueous 16,5% wt. NaOH introduced to the extraction process as phenol extractant resulted from the stoichiometry of the phenol-NaOH reaction. Figure 3 shows that the extraction efficacy decreases with the increase of the hydrocarbon fraction flow through the membrane module. For lower hydrocarbon fraction flows of about 50 L/h, the degree of dephenolization of the organic fraction was very high - about 99%. For a substrate stream of up to
86 L/h, the degree was still high of the level of 90%. In the experiments with the fraction flows through the module of about 100 L/h the efficiency of the extraction process decreased to 85%. So the decrease of the substrate flow enables increase of the process efficacy but it implies the necessity of arranging greater number of the membrane modules, thus increasing the investment costs.

It was found that the process of extraction of phenol with the aqueous NaOH is realised not only by the soda lay but also by the sodium phenolate formed in the chemical reaction of phenol and NaOH. In some of our experiments the amount of the soda lay introduced to the process was below stoichiometric demand. It was observed that in these cases the decrease of the process efficiency was smaller than it was presumed on the basis of the reaction of phenol and NaOH. To assess the influence of the additional process a test was performed with an aqueous sodium phenolate 38 % wt. solution as the only extractant. There was no free NaOH in the extractant used in the test. The volume of the substrate stream was kept stable in the test – 50 l/h. During the test only the amount of extractant introduced to the membrane module was varied. The test results are shown in Fig. 4.

![Fig. 4. Phenol extraction with aqueous 38% wt. sodium phenolate](image)

The phenolate solution stream flow was varied from 1.6 L/h to 4.2 L/h. In these conditions the experimental degree of dephenolization of the crude hydrocarbon fraction was 26% for the lowest flow of the phenolate solution to as high as 43% for the highest flow of the extractant. This finding is considered advantageous for the whole extraction process. It enables certain reduction in the NaOH consumption in the process. We presume that the amount of NaOH consumed in the process can be lower than it results from the stoichiometry of the phenol – NaOH reaction.

**LAUNCHING of the PROCESS**

Fig. 5 shows a block diagram of a plant for extractive dephenolization of the hydrocarbon fraction. The stream of 650 kg/h of filtered crude hydrocarbon fraction containing 2-4 % wt. of phenol is fed into the tube side of the membrane fibers of the first stage extractor and than it is similarly fed to the tube side of the second stage extractor. Each extraction stage comprises 8 modules of 4”x28” arranged parallel. The characteristic of the modules is given in Table 3. In the first extraction stage the crude hydrocarbon fraction is subjected to partial dephenolization (to about 0.4-0.6 % wt.) and free NaOH present in the extracting solution is totally consumed. The final
dephenolization (down to 0.02 % wt.) is carried out in the second extractor fed with fresh aqueous NaOH.

**Fig. 5.** Scheme of launched extraction process.

In each of the extraction stages an aqueous extracting solution of various NaOH and sodium phenolate content is fed into the shell side of the membrane modules. The aqueous phase flow is countercurrent to the organic phase flow. The volume of the extraction solution fed to the membrane modules (circulation) corresponds to 50% of the volume of the treated hydrocarbon fraction stream. The extraction mixture tank is divided into two chambers with a wall. The excess of the extraction mixture leaves the right chamber and flows to the left second one. The level of the mixture in the left chamber is automatically controlled. The excess of the aqueous solution (final phenolate) makes a by-product of the process and it is utilised in the process of technological stream neutralisation. Dephenolized hydrocarbon fraction makes the main product of the membrane extraction plant. It is recycled to the main synthesis process where after the distillation and reaction process it enriches the cumene stream.

Fig. 6 shows the degree of the hydrocarbon fraction dephenolization vs. the volume of the organic stream subjected to the extraction process. The degree of dephenolization has been calculated according to the analysis of phenol content in the second extraction stage product with stoichiometric consumption of NaOH in the dephenolization process. Crude hydrocarbon fraction contained about 3.0% wt. of phenol. Fig. 6 shows that the greater the volume of the stream, the lower the degree of dephenolization. For 700 L/h stream the degree of dephenolization was as high as 99.5% while the phenol content in the processed stream was below 0.02% wt.

Elevation of the stream feed to 800 L/h resulted in reduction of the dephenolization process efficiency to 98.5% and it corresponded to phenol content in the final processed stream of about 0.05% wt. The pilot plant experiments final degree of dephenolization was about 90% (Fig. 3) for a crude hydrocarbon stream of 85 L/h (one module, no streams circulation). For the full-scale process and the same fraction flow (calculated per one module) the efficiency of phenol extraction was higher (99.2%, see Fig. 6). It was due to the two-stage arrangement of the extraction process and to application of the circulation of the aqueous streams in the technology.
Fig. 6. Dephenolization degree vs. hydrocarbon fraction flow.

Fig. 7 shows that the phenol content in the raffinate after the first stage of the extraction strictly depends on its content in the hydrocarbon fraction substrate. It was about 0.4% wt. for a substrate containing 2.7% wt. of phenol and it was as high as 1.6% wt. for the one containing more than 4.0% wt. of phenol. The data were gained for an organic stream of 685 L/h.

Fig. 7. The relationship between phenol content in the hydrocarbon feed and its content in the raffinate after the first stage of the extraction.

The hydrocarbon fraction partly dephenolized in the first extraction stage was directly introduced to the modules of the second extraction stage. Fig. 8 shows the phenol content change in the final organic product with its content in the partially dephenolized substrate (raffinate from first stage).

In the commercial process the phenol content in the crude hydrocarbon fraction stream varies in the range of 2-4% wt. Thus the concentration of phenol in the second extraction stage feed has varied as well (Fig. 7). Fig. 8 shows that the variations have only slight influence on the quality of the final product.
The phenol content in the final product has been in the range of 0.01 – 0.03 % wt. This finding shows that the second stage of the extraction process is highly effective. According to our analysis 97 – 98 % of phenol introduced into the second stage of the process has effectively been removed.

**FINAL REMARKS**

The extraction process was launched at PKN ORLEN, Plock, in March 2003. Pictures 1 and 2 show the full-scale installation. It is worth mentioning that the whole plant takes as little area as about 6 m².

**Fig.8.** Second extraction stage – phenol content in the final organic product vs. its content in the partially dephenolized hydrocarbon fraction.

**Pict.1.** General view of the industrial installation for dephenolization of the hydrocarbon fraction.
No objection of the plant staff regarding operation of the installation has been reported. The typical process parameters are in the ranges as follows:


Phenol content in (% wt.): hydrocarbon fraction feed - 2,5-3,5; hydrocarbon fraction after I stage - 0,4-1,0; hydrocarbon fraction product - below 0,02; final aq. sodium phenolate - 25-30.

Aqueous phase side overpressure applied in membrane module - 20-30 kPa

In conclusion:
- Extractive dephenolization of the hydrocarbon fraction with aqueous NaOH on the membrane installation is a highly effective process;
- No hydrodynamic problems have been observed. The technological streams produced in the process are mono-phase and clear;
- Phenol content in the final product depends mainly on the flow rate of the dephenolized hydrocarbon fraction stream calculated per 1 membrane module (it should be below 100 L/h) as well as on the concentration of phenol in the crude substrate;
- Circulation of the extracting mixture i.e. aqueous NaOH and sodium phenolate solution is considered favourable. It increases extraction of phenol due to some extractive capabilities of the sodium phenolate solution.