

On the basis of research studies and an analysis of schemes for processing unsaturated gas to obtain propylene, we can propose the following combined scheme for treating unsaturated refinery gas (Fig. 1). Wet gas from catalytic and thermal cracking, dry gas, and the GFU stabilizer head cut (C₃-C₄) are treated with monoethanolamine to remove hydrogen sulfide. The MEA solution from all of the adsorbers is regenerated in a single vessel. The C₃-C₄ cut, with hydrogen sulfide content below 0.001% by weight, is treated to remove mercaptans by the VNIUS-12 method.

The propane-propylene cut from the GFU is mixed with PPC from outside, and this mixture is fed to the VNIUS-12 unit for a final treatment to remove mercaptans and carbonyl sulfide. The catalyst complex from the extracts obtained in this unit is also regenerated in a single regenerator. Then the PPC is dried on A-1 aluminum oxide. The adsorbent is regenerated by dry gas from the GFU that has been treated to remove hydrogen sulfide. The regeneration gas is used as process fuel.

This combined treating scheme offers a means for producing, from unsaturated refinery gas, a concentrated propylene (conforming to GOST 25043-81) and BBC with a content of organic sulfur compounds no greater than 0.003% by weight. It also makes it possible to curtail, by a factor of more than 10, the consumption of caustic and the quantity of sour caustic waste produced in sulfur removal from unsaturated gas, in comparison with the treating schemes currently used; also, the consumption of sulfuric acid in the alkylation unit is reduced significantly.

LITERATURE CITED

1. A. G. Akhmadullina, L. N. Orlova, G. M. Nurgaleeva, et al., in: Improvement of Processes of Sulfur Removal from Hydrocarbon Feedstocks and Gas Fractionation [in Russian], TsNIITÉneftkhim, Moscow (1980), pp. 158-162.
2. A. M. Mazgarov, A. V. Neyaglov, É. Sh. Telyakov, et al., Khim. Tekhnol. Topl. Masel, No. 12, 6-8 (1976).
3. USSR Inventor's Certificate 823,418.
4. A. Z. Dorogochinskii, A. V. Lyuter, E. G. Vol'pova, et al., Sulfuric Acid Alkylation of Isoparaffins by Olefins [in Russian], Khimiya, Moscow (1970), p. 65.
5. USSR Inventor's Certificate 882,586.

PHASE COMPOSITION OF SOLVENTS IN DEOILING UNITS

V. P. Varshaver, A. K. Manovyan,
V. V. Lozin,* and G. P. Kavyrshina

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The solvents used in deoiling units are complex mixtures of ketones and aromatic hydrocarbons with small amounts of water. These solvents form heteroazeotropic mixtures with water. Because of the high solubility of water in these solvents, the content of ketone in the mixture must be held below the optimum level, and this has an adverse effect on the wax yield and quality [1, 2].

The water is separated from the mixture of solvents, in which it has a limited solubility, by azeotropic distillation in a two-tower system [3]. In order to calculate such towers, experimental data are needed on the composition of the vapor and liquid phases of the complex solvents.

Our investigation of the phase compositions included three stages: development of a procedure for determining the content of water in the solvents; determination of the vapor/liquid phase equilibrium curve in laboratory apparatus and a check of calculations; simulation of

*Deceased.

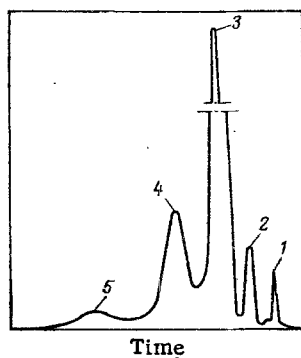


Fig. 1

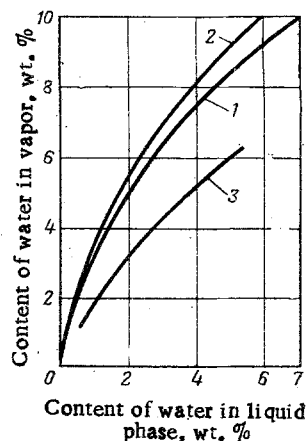


Fig. 2

Fig. 1. Chromatogram of MEK-toluene-acetone-water-benzene solvent: 1) water; 2) acetone; 3) MEK; 4) benzene; 5) toluene.

Fig. 2. Curves for equilibrium distribution of water between liquid and vapor phases of solvents: 1) 73% MEK, 27% toluene; 2) 67% MEK, 33% toluene; 3) 68% MEK, 32% acetone.

TABLE 1

| Equilibrium composition, mole fraction | | | | Temperature, °C | Vapor pressure of pure component, kPa | | | Calculated value of activity coefficient | | Mean values of constants | |
|--|-------|-------------|-------|-----------------|---------------------------------------|---------|------------|--|---------|--------------------------|--|
| liquid phase | | vapor phase | | | p_1^0 | p_2^0 | γ_1 | γ_2 | A_1 | A_2 | |
| x_1 | x_2 | y_1 | y_2 | | | | | | | | |
| MEK-acetone [6] | | | | | | | | | | | |
| 0,755 | 0,245 | 0,563 | 0,437 | 71,4 | 77,22 | 161,97 | 0,976 | 1,113 | } 0,078 | 0,034 | |
| 0,627 | 0,373 | 0,429 | 0,571 | 69,0 | 71,02 | 150,27 | 0,974 | 1,030 | | | |
| 0,490 | 0,510 | 0,343 | 0,657 | 65,1 | 62,72 | 133,48 | 1,128 | 0,975 | | | |
| Acetone-water [6] | | | | | | | | | | | |
| 0,176 | 0,824 | 0,805 | 0,195 | 63,0 | 124,44 | 23,24 | 3,715 | 1,029 | } 0,790 | 0,902 | |
| 0,330 | 0,670 | 0,837 | 0,163 | 60,9 | 115,41 | 20,88 | 2,221 | 1,178 | | | |
| 0,461 | 0,539 | 0,848 | 0,152 | 59,8 | 110,97 | 19,79 | 1,675 | 1,440 | | | |
| 0,024 | 0,976 | 0,466 | 0,534 | 85,1 | 241,84 | 60,99 | | | | | |
| MEK-water [6] | | | | | | | | | | | |
| 0,036 | 0,964 | 0,618 | 0,382 | 75,5 | 89,12 | 39,97 | 19,470 | 1,002 | } 1,16 | 1,05 | |
| 0,190 | 0,810 | 0,645 | 0,355 | 74,4 | 85,93 | 38,20 | 3,993 | 1,160 | | | |
| 0,721 | 0,279 | 0,676 | 0,324 | 73,8 | 84,18 | 37,23 | 1,126 | 3,153 | | | |
| 0,800 | 0,200 | 0,707 | 0,293 | 73,0 | 81,86 | 35,94 | 1,091 | 4,120 | | | |

TABLE 2

| Liquid phase, mole fraction | | | Vapor phase, mole fraction | | | | | | Relative error of calculation, % | | |
|-----------------------------|---------------|-------------|----------------------------|---------------|-------------|-----------------|----------------|--------------|----------------------------------|--------------------------|--------------------------|
| MEK X_1 | acetone X_2 | water X_3 | experimental data | | | calculated data | | | $\frac{Y_1 - Y_1'}{Y_1}$ | $\frac{Y_2 - Y_2'}{Y_2}$ | $\frac{Y_3 - Y_3'}{Y_3}$ |
| | | | MEK Y_1 | acetone Y_2 | water Y_3 | MEK Y_1' | acetone Y_2' | water Y_3' | | | |
| 0,2902 | 0,6358 | 0,074 | 0,343 | 0,530 | 0,127 | 0,422 | 9,576 | 0,09 | 2,30 | 7,90 | 29,10 |
| 0,3190 | 0,571 | 0,110 | 0,396 | 0,457 | 0,147 | 0,417 | 0,463 | 0,118 | 5,30 | 1,32 | 19,72 |
| 0,3400 | 0,580 | 0,070 | 0,423 | 0,476 | 0,101 | 0,451 | 0,486 | 0,076 | 6,62 | 2,1 | 24,75 |
| 0,2750 | 0,597 | 0,128 | 0,347 | 0,476 | 0,177 | 0,363 | 0,488 | 0,138 | 4,61 | 2,52 | 22,03 |

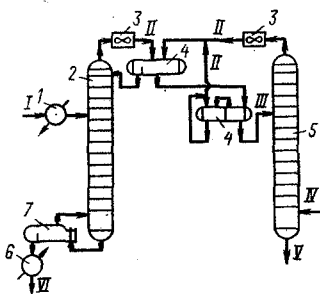


Fig. 3. Flow plan for drying solvents: 1, 7) steam preheaters; 2) drying tower; 3) air coolers; 4) tank; 5) ketone tower; 6) condenser-cooler; I) wet solvent (feed to drying tower); II) solvent with water (distillate); III) feed to ketone tower; IV) steam; V) water; VI) dry solvent.

the operation of a distillation tower for removal of the water from the solvent with the overhead product.

The content of water in the solvents was determined by the use of Fischer reagent, cobalt chloride, and calcium carbide, and was also determined chromatographically on various packings [4] and by other methods. As column packing we tested, for example, 0.5% (wt.) polyethylene glycol 400 on sodium chloride or Chromosorb W, 5% squalane on Chromosorb W, and 5% polyethylene glycol adipate on Polysorb 1. We found that inert adsorbents are capable of adsorbing and retaining water; and as a consequence, the results of the analysis are not reproducible. We were able to eliminate this phenomenon completely by choosing certain conditions of analysis in an LKhM-8MD chromatograph: column length 2 m, temperature 170-175°C, carrier gas (nitrogen) flow rate 80-85 ml/min, vaporizer temperature 250°C, sample size 1-1.5 μ l. The packing was prepared as follows: Polysorb 1 was held for 3 h in a thermostat (0.002 MPa, 110-120°C); then, 5% polyethylene glycol adipate (relative to the packing weight) was applied to the solid support. The time required for analysis of the five-component mixture (water, acetone, methyl ethyl ketone, benzene, and toluene) was 2.5-3 min. A chromatogram of a typical mixture is shown in Fig. 1. Calibration coefficients were determined on artificial mixtures of thoroughly dried c.p. components.

The phase equilibrium of the multicomponent solvents was investigated in a specially developed laboratory apparatus with precise temperature control and good repeatability of the results of analysis. The composition of the phases of the MEK-toluene-water and MEK-acetone-water mixtures was determined with various contents of water (Fig. 2). With increasing content of water in the liquid phase, its content in the vapor phase increases, the amount of this increase depending on the composition of the original mixture. Thus, when the MEK content in the liquid phase of the MEK-toluene mixture is lowered (Fig. 2, curve 2), the content of water in the vapor increases slightly. When the toluene is replaced by acetone, the increase in the quantity of water in the vapor is somewhat less (Fig. 2, curve 3). With a constant content of water (2.5%), an increase in the content of MEK in the mixture with toluene from 65% to 80% leads to an increase in the content of MEK in the vapor phase from 76% to 82% by weight.

The experimental data were worked up by the use of the third-order equation of Margules [5]. In calculating the activity coefficients of the components, we used data on the compositions of the binary mixtures [6] (Table 1). The agreement between the calculated results and the experimental data is satisfactory (Table 2), so that the data required for the design of the distillation towers can be obtained by calculation.

Experimental data on the maximum removal of water from multicomponent selective solvents were obtained by distilling the solvents in a continuous flow plan (Fig. 3, tower 2). Laboratory modeling of this flow plan was accomplished by the use of an RUST-1 fractionating column, made of heat-resistant glass [7] with a diameter of 30 mm, equipped with 12 bubble-cap plates.

TABLE 3

| Index | Experiment | | |
|-----------------------|------------|-------|-------|
| | 1 | 2 | 3 |
| Temperature, °C | | | |
| tower top | 75 | 77 | 76 |
| reflux | 45 | 45 | 45 |
| feed inlet | 75 | 75 | 74 |
| tower bottom | 82 | 84 | 84 |
| in tower still | 93 | 95 | 95 |
| Flow rate, kg/h | | | |
| feed | 0.76 | 0.66 | 0.76 |
| reflux (second feed) | 0.48 | 0.65 | 0.74 |
| distillate | 0.46 | 0.46 | 0.53 |
| residue (dry solvent) | 0.78 | 0.85 | 0.98 |
| Composition, wt. % | | | |
| feed | | | |
| MEK | 68.05 | 72.0 | 69.1 |
| toluene | 29.07 | 24.7 | 28.5 |
| water | 2.88 | 3.3 | 2.4 |
| reflux | | | |
| MEK | 70.0 | 71.0 | 69.1 |
| toluene | 25.6 | 24.7 | 27.5 |
| water | 4.4 | 4.3 | 3.4 |
| distillate | | | |
| MEK | 77.9 | 78.5 | 76.6 |
| toluene | 14.0 | 15.1 | 17.5 |
| water | 7.1 | 7.4 | 5.9 |
| residue | | | |
| MEK | 68.0 | 67.7 | 66.95 |
| toluene | 31.84 | 32.15 | 32.91 |
| water | 0.16 | 0.15 | 0.14 |

The conditions were chosen to model the drying of a wet solvent used in deoiling processes, a mixture of 72% MEK and ~28% toluene. The column was fed from a Mariotte bottle through a rotameter, onto the 10th plate from the top. In the vapor leaving the top of the column, the water content was 6-7%, and in the residue 0.14-0.16%, with a standard of 0.2% (all percentages by weight) (Table 3).

Thus, we have demonstrated the feasibility of drying this solvent by azeotropic distillation and have defined more precisely the material balances of both states in the distillation. These results have been used in drawing up instructions governing the design of the MEK-toluene solvent deep-drying section for a commercial wax deoiling unit. The design capacity of the section is 720 metric tons of solvent per day. It consists of two towers (see Fig. 3): a solvent drying tower (diameter 2.2 m, 18 trays), and a tower for distilling the MEK from the water (diameter 0.5 m, 18 trays). The content of water in the dried solvent is no greater than 0.2% by weight.

LITERATURE CITED

1. L. P. Kazakova and S. É. Krein, *Physicochemical Principles of Petroleum Oil Manufacture* [in Russian], Khimiya, Moscow (1978).
2. A. N. Pereverzev, N. F. Bogdanov, and Yu. N. Roshchin, *Production of Paraffin Waxes* [in Russian], Khimiya, Moscow (1973).
3. S. V. L'vov, *Certain Problems in the Distillation of Binary and Multicomponent Mixtures* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1960).
4. A. Yu. Bruk, B. I. Turbina, and V. I. Markova, *Neftepererab. Neftekhim. (Moscow)*, No. 7, 28-29 (1975).
5. E. Hala et al., *Vapour-Liquid Equilibrium*, 2nd edn., Pergamon Press, New York (1968).
6. B. V. Kogan, V. M. Fridman, and V. V. Kafarov, *Equilibrium between Liquid and Vapor* [in Russian], Nauka, Moscow (1966).
7. USSR Inventor's Certificate 559,715.