

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.

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PHASE COMPOSITION OF SOLVENTS IN DEOILING UNITS

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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

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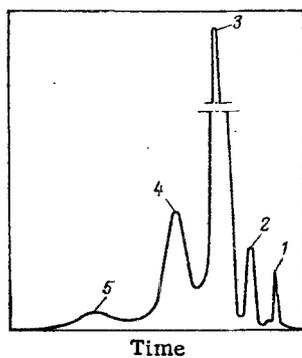


Fig. 1

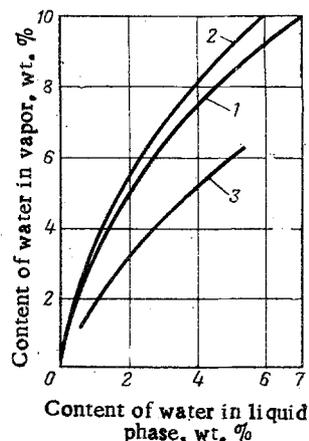


Fig. 2

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

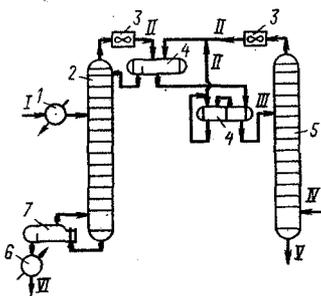


Fig. 3. Flow plan for drying solvents: 1, 7) steam preheaters; 2) drying tower; 3) air coolers; 4) tank; 5) ketone tower; 6) condenser-cooler; I) wet solvent (feed to drying tower); II) solvent with water (distillate); III) feed to ketone tower; IV) steam; V) water; VI) dry solvent.

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.

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