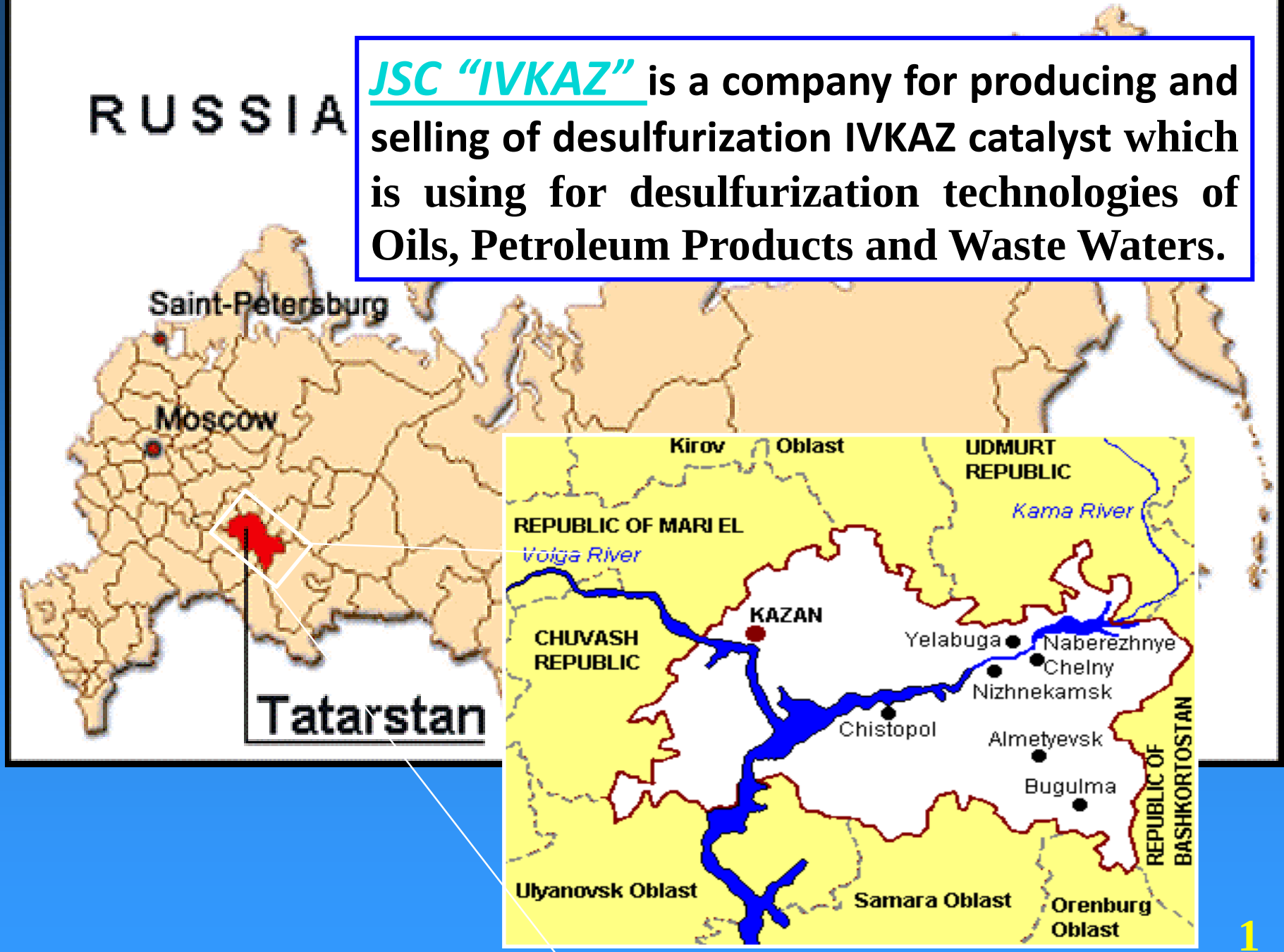
Technologies for treating Oils, Petroleum Products and Waste Waters for sulfur compounds using Desulfurization IVKAZ catalyst

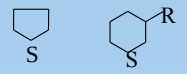
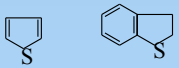
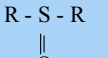
JSC «IVKAZ»

Vostaniya str., 100, Kazan, 420095 Russia
Tel: +7(843) 212-51-46, +7(843) 295-35-16, Fax: +7(843) 253-69-76; +7(843)272-40-93
www.ivkaz.com E-mail: tiol.zao@gmail.com; info@tiol-kazan.com

JSC "IVKAZ" is a company for producing and selling of desulfurization IVKAZ catalyst which is using for desulfurization technologies of Oils, Petroleum Products and Waste Waters.



Sulfur compounds of crude oil

Chemical formula	Name	T_{boil}	Notes
S^0	Elemental Sulfur	134 ^{0}C (T_{melt})	Active Sulfur
H_2S	Hydrogen sulfide	- 60,7 ^{0}C	
COS	Carbonyl Sulfide	- 47,5 ^{0}C	
RSH	Mercaptans (thiols)	6÷500 ^{0}C	
CS_2	Carbon disulfide	46,3 ^{0}C	
R-S-R, Ar-S-R, Ar-S-Ar	Sulfides (thioethers)	35÷600 ^{0}C	
			
R-S-S-R, Ar-S-S-R	Disulfides	109÷600 ^{0}C	
	Thiophenes	84÷600 ^{0}C	Residual Sulfur
	Sulfoxides		
	Sulfones		

Maximum Permissible Concentration of Mercaptans (MPC)

Mercaptans	T_b, ^0C	$MPC_{W.Z.}$ mg/m^3	$MPC_{M.S.}$ mg/m^3	Odour threshold mg/m^3
CH_3SH Methyl mercaptan	+ 6	0.8	$9 \bullet 10^{-6}$	$2 \bullet 10^{-5}$
C_2H_5SH Ethyl mercaptan	+ 36	1.0	$3 \bullet 10^{-5}$	$6 \bullet 10^{-5}$
$i - C_3H_7SH$ i-Propyl mercaptan	+ 60	1.5	$1 \bullet 10^{-4}$	$2 \bullet 10^{-4}$
H_2S Hydrogen sulfide	- 61	10	$8 \bullet 10^{-3}$	$1.2 \bullet 10^{-5}$

Total Sulfur and Mercaptan Sulfur Content in Different Crude Oils and Condensates

Charge Stock	Total Sulfur, Wt %	Mercaptan Sulfur , Wt %	MeSH, ppm	EtSH, ppm	Methyl and Eth. Mercaptan ppm
Astrakhan Condensate	1.38	0.19	340	270	610
Orenburg Condensate	1.25	0.84	15	400	415
Karachaganak Condensate	0.67	0.16	135	460	595
Tengiz Crude	0.58	0.08	150	200	350
Zhanazhol Crude Oil	0.47	0.18	42	213	255
Qatar Condensate	0.26	0.17	17	313	330
Douglas Crude (Great Britain)	0.40	0.13	5	50	55
South Pars Condensate (Iran)	0.67	0.15	150	350	500
Yamashi Crude (Tatarstan)	3.10	0.14	6	68	74
Markovskii Crude (Irkutsk Obl.)	1.00	0.41	35	85	120
Novolabitski Crude (Ul`yanovsk Obl.)	4.58	0.35	25	225	250
Radaevskii Crude (Samara.Obl.)	3.05	0.078	10	55	65
Shchelkanovskii Crude (Bashkortostan)	4.45	0.054	6	50	56
Noshovskii Crude (Perm` Obl.)	3.40	0.067	8	50	58

Why treatment of crude oil and gas condensate for hydrogen sulfide and mercaptans C_1-C_2 is necessary?

- *Hydrogen sulfide and C_1-C_2 mercaptans are very toxic, have very unpleasant odour and high volatility (b.p. of methyl mercaptan is 6 ^{0}C, b.p. of ethyl mercaptan is 35 ^{0}C). Their presence in oils creates ecological problems during transportation and storage of oil, especially during transferring this feedstock.*

- *Hydrogen sulfide and C_1-C_2 mercaptans cause corrosion of pipelines and storage system during oil transportation and processing.*

- *Hydrogen sulfide and C_1-C_2 mercaptans are soluble in water (solubility of methyl mercaptans is up to 3.0 % vol.) and cause problems, when treating waste waters from tanks and electric desalting plants during oil processing.*

- *Experience of Russian refineries shows that mercaptans cause accelerated coking on the surface of catalyst bed in reactors of fraction IB-180^{o}C hydrotreating because of a high velocity of their thermal decomposition at temperatures as low as 220−250^{o}C.*

Why treatment of crude oil and gas condensate for hydrogen sulfide and mercaptans C_1-C_2 is necessary?

Chevron company, the Russian oil companies and Chinese oil company CNPC in Kazakhstan

treat crude oil for hydrogen sulfide up to 10 ppm

and mercaptans C_1-C_2 up to 20 ppm using

the DMC technologies.

The treatment of oil with usage of ***DMC processes*** reduces a corrosion activity of feedstock twice, allows to produce LPG without subsequent treatment for sulfur compounds (if during oil refining the secondary mercaptans C_1-C_2 will not be formed because of decomposition of other sulfur compounds).

MECHANISM OF MERCAPTAN OXIDATION REACTION

$$RSH + NaOH \leftrightarrow RSNa + H_2O$$

$$RSNa \leftrightarrow RS^- + Na^+$$

$$Kt + O_2 \leftrightarrow [Kt....O_2]$$

$$[Kt....O_2] + RS^- \rightarrow RS^\bullet + Kt + O_2^{\bullet -}$$

$$RS^\bullet + RS^\bullet \rightarrow RSSR$$

$$Kt + RSSR \leftrightarrow [Kt....RSSR]$$

$$O_2^{\bullet -} + H_2O \rightarrow 2OH^- + 0{,}5O_2$$

$$OH^- + Na^+ \leftrightarrow NaOH$$

Chemistry of DMC process

$$H_2S + 2NaOH \rightarrow Na_2S + 2H_2O$$

$$H_2S + 2\,NH_4OH \leftrightarrow NH_4HS \cdot NH_4OH + H_2O$$

$$R`COOH + NaOH \rightarrow R`COONa + H_2O$$

$$RSH + NaOH \rightarrow RSNa + H_2O$$

$$3Na_2S + 4O_2 + H_2O \xrightarrow{Kt} Na_2S_2O_3 + Na_2SO_4 + 2NaOH$$

$$NH_4HS + 0.5\,O_2 \xrightarrow{Kt} S + NH_4OH$$

$$2RSNa + 0{,}5O_2 + H_2O \xrightarrow{Kt} RSSR + 2NaOH$$

$$-r_{RSNa} = \frac{K_1 Kp[RS][Kt][O_2]}{1+Kp[O_2]+K_2[RSSR]}$$

Desulfurization IVKAZ catalyst

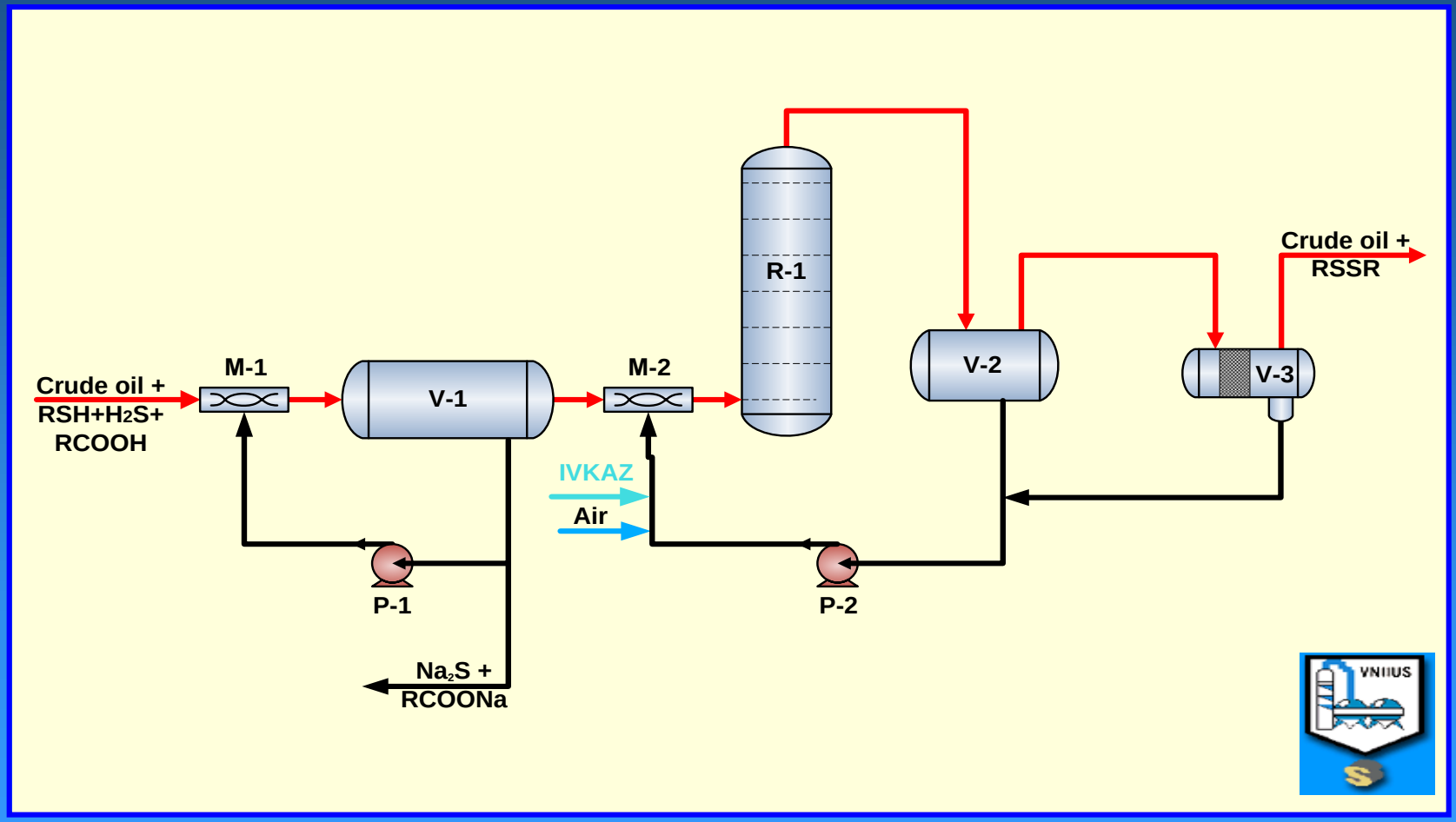
Cobalt Phthalocyanine

R = - SO_3H^-, Cl^-, OH^-, Br^-

R_1 = $PhCH_2^-$, NO_2^-, NH_2^-

DMC-1 PROCESS

for treating light oils and gas condensates for hydrogen sulfide (from 100 to 5 ppm) and low molecular weight mercaptans $C_1 – C_2$(from 600 to 20 ppm)



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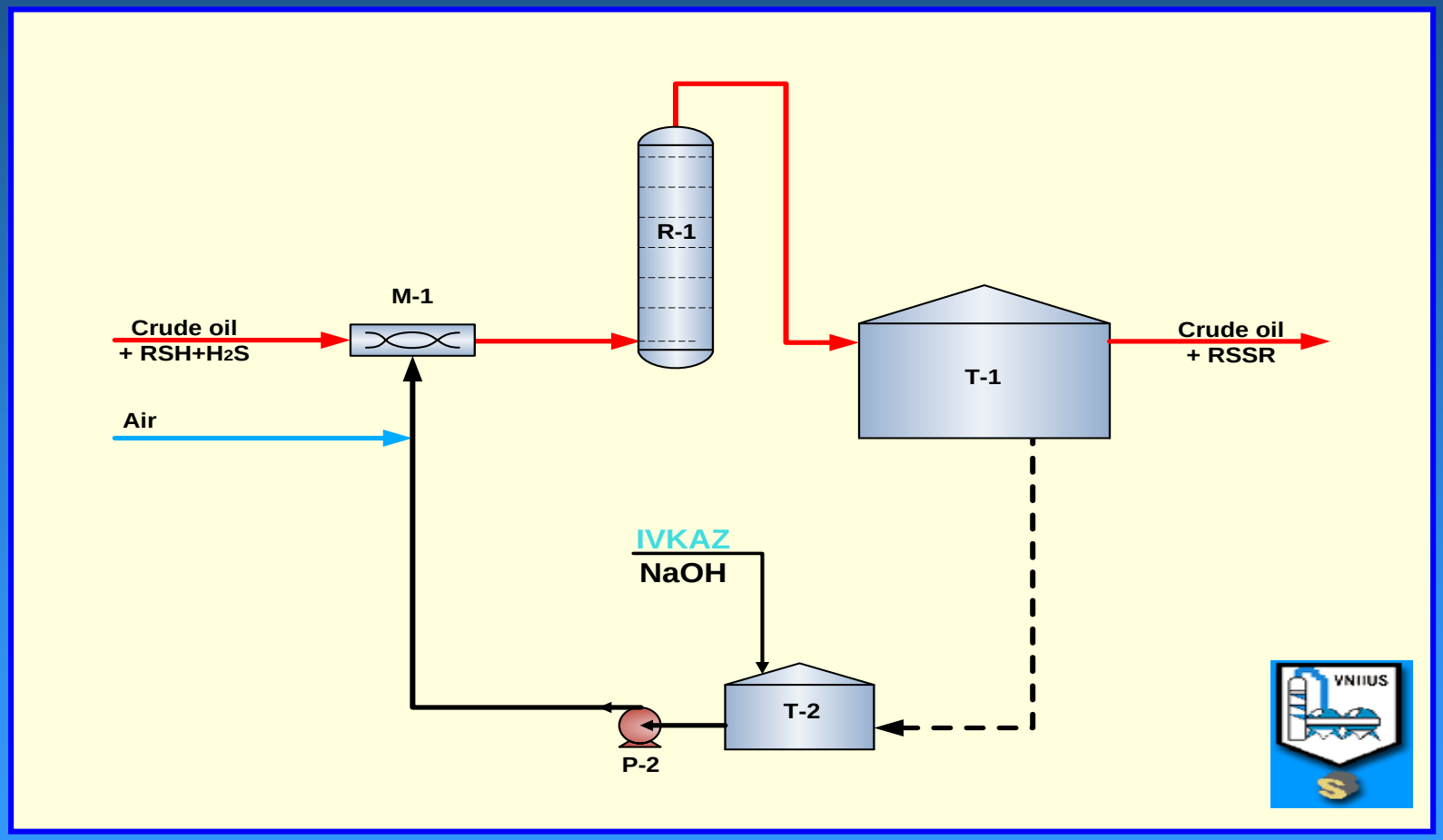
DMC-1 plant in Tengiz Gas Refinery

DMC-1M PROCESS

for selective treating heavy oils and gas condensates for low molecular weight mercaptans C1 — C2 (from 300 to 20 ppm) and hydrogen sulfide (from 100 to 5 ppm), which form stable emulsions when contacting alkaline solutions.



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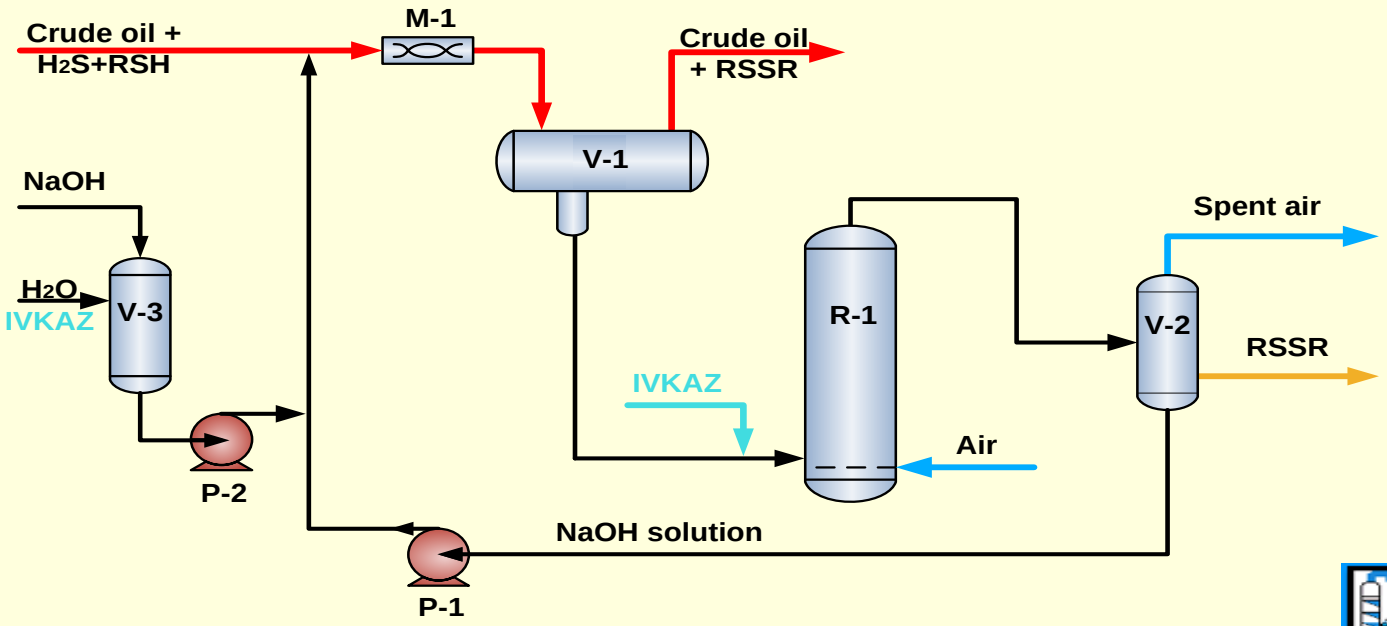
Chemistry of DMC – 1M process

1. $2\,NaOH + H_2S \rightarrow Na_2S + 2H_2O$
2. $NaOH + H_2S \rightarrow NaHS + H_2O$
3. $NaHS + O_2 \xrightarrow{Kt} S^0 + NaOH$
4. $2Na_2S + 2O_2 + H_2O \xrightarrow{Kt} Na_2S_2O_3 + 2NaOH$
5. $2Na_2S + 2O_2 \xrightarrow{Kt} Na_2SO_3 \rightarrow Na_2SO_4$
6. $RSH + NaOH \rightarrow RSNa + H_2O$
7. $RSH + S^0 \rightarrow RSSR + H_2S_2$
8. $2RSNa + O_2 + H_2O \xrightarrow{Kt} RSSR + 2NaOH$
9. $CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$
10. $Na_2CO_3 + CaCl_2 \rightarrow CaCO_3\downarrow + 2NaCl$
11. $RCOOH + NaOH \rightarrow RCOONa + H_2O$
12. $2RCOONa + CaCl_2 \rightarrow (RCOO)_2Ca + 2NaCl$

DMC-2 PROCESS

for selective light oil treatment for hydrogen sulfide and low-molecular weight mercaptans C1-C2 without the oil contact with the air



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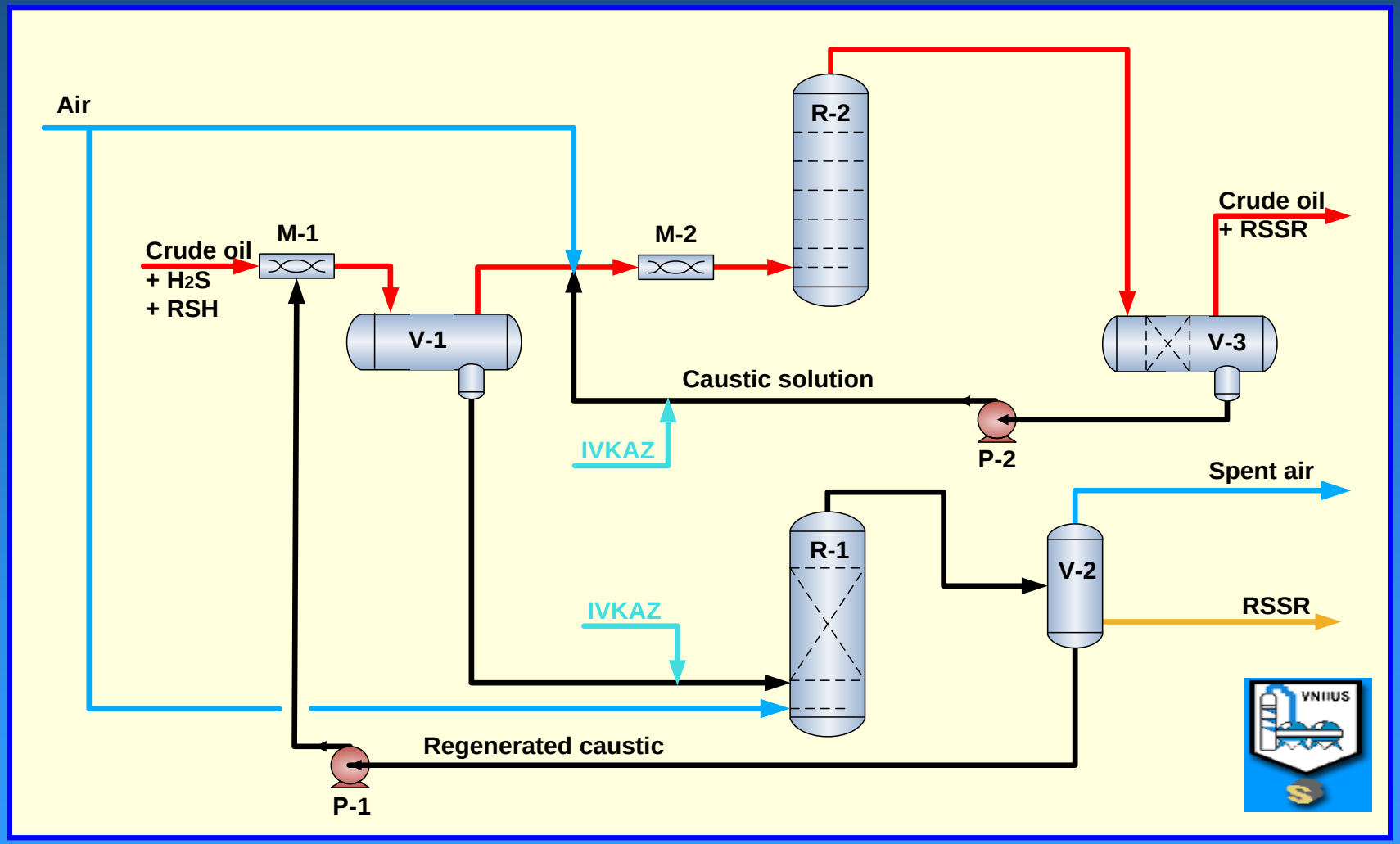
DMC-3 PROCESS

for treating oils and gas condensates for hydrogen sulfide (from 100 to 5 ppm) and low molecular weight mercaptans $C_1 – C_4$(from 4000 to 50 ppm)



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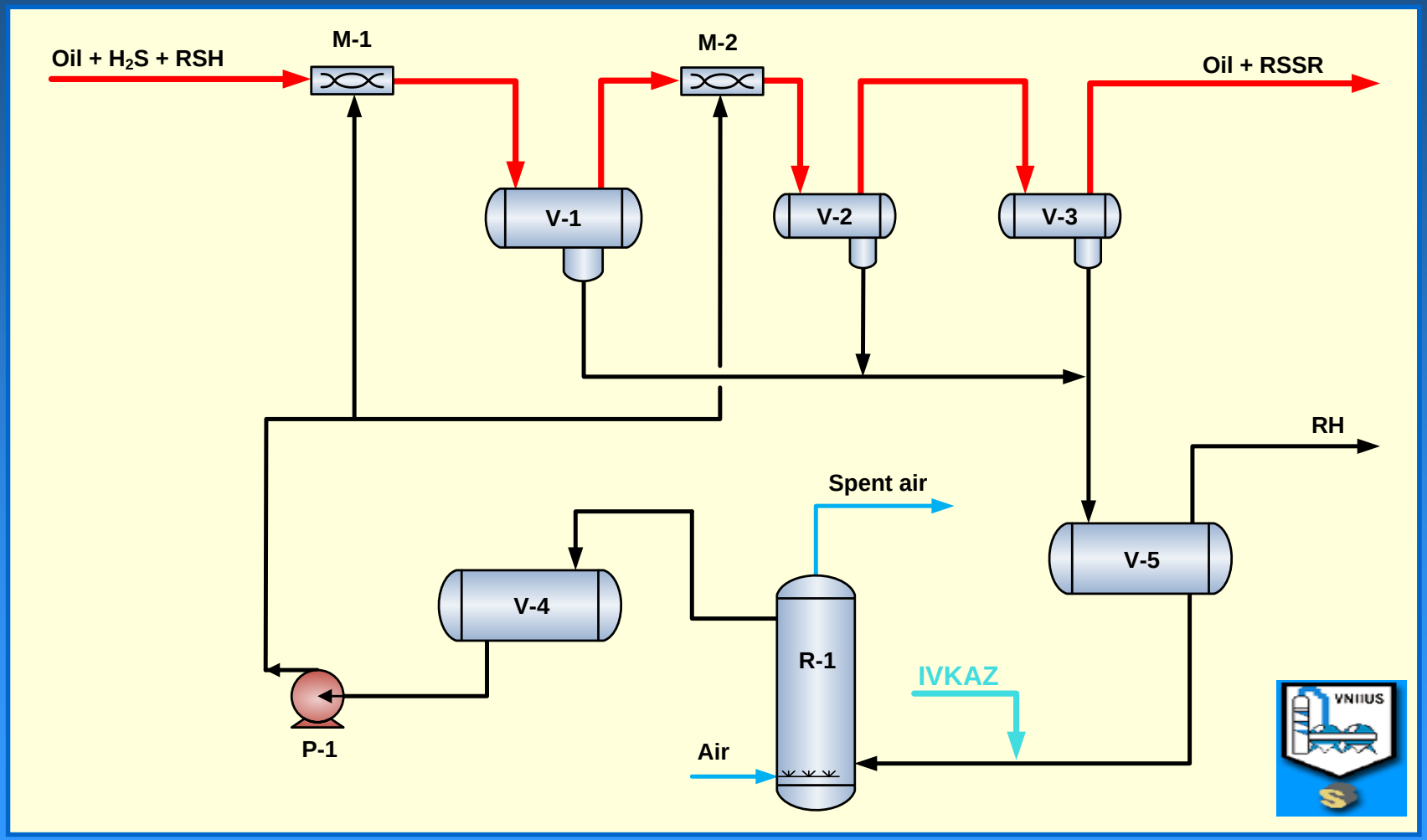
DMC-4 PROCESS

for treating heavy oils and gas condensates for low molecular weight mercaptans C1 — C2 (from 300 to 20 ppm) and hydrogen sulfide (from 100 to 5 ppm) on oil fields.



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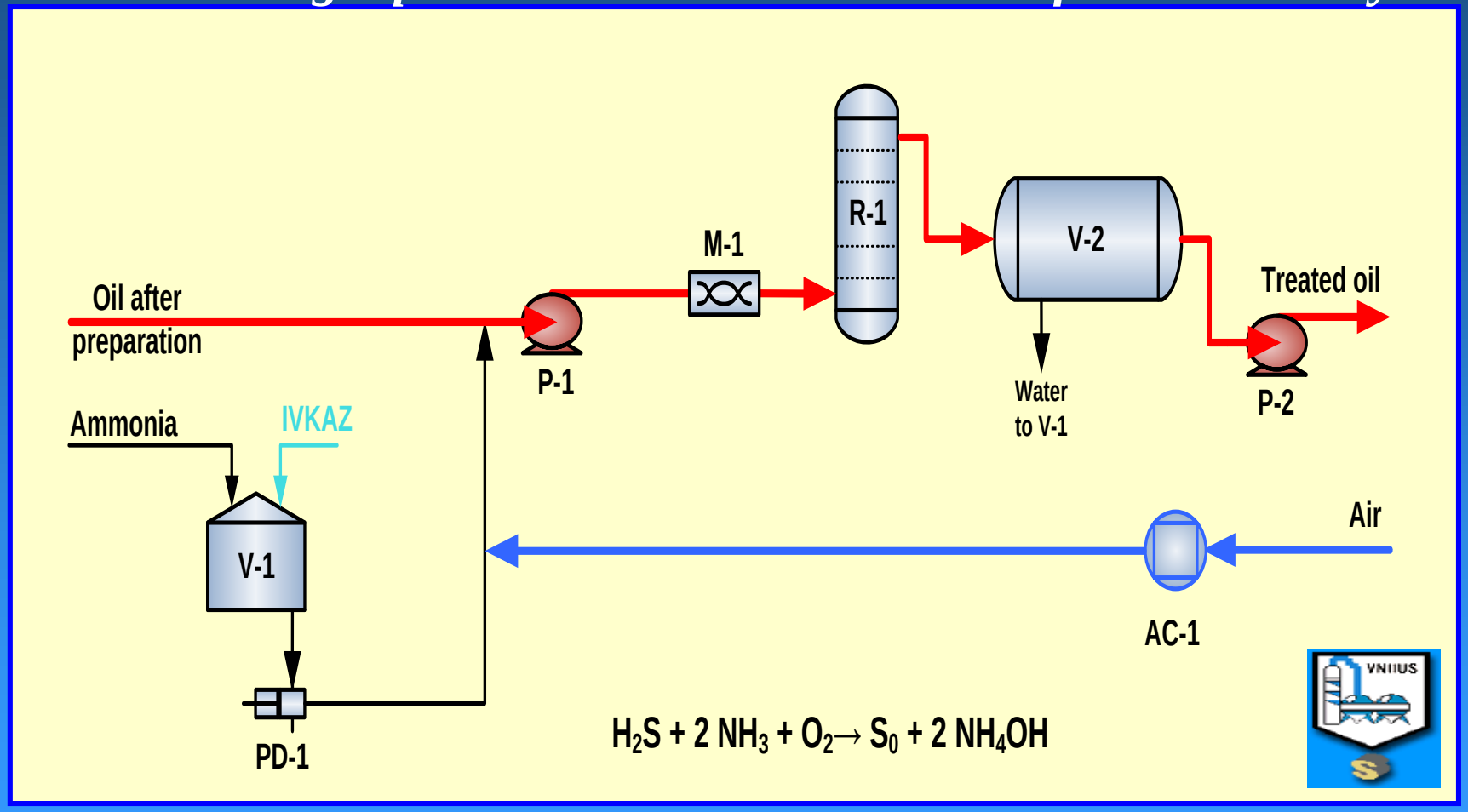
DMC-1MA PROCESS

The most efficient and economic process for treating oil with high content of hydrogen sulfide (from 500 ppm to 5 ppm) is liquid-phase oxidation using aqueous-ammonium solution of IVKAZ catalyst.



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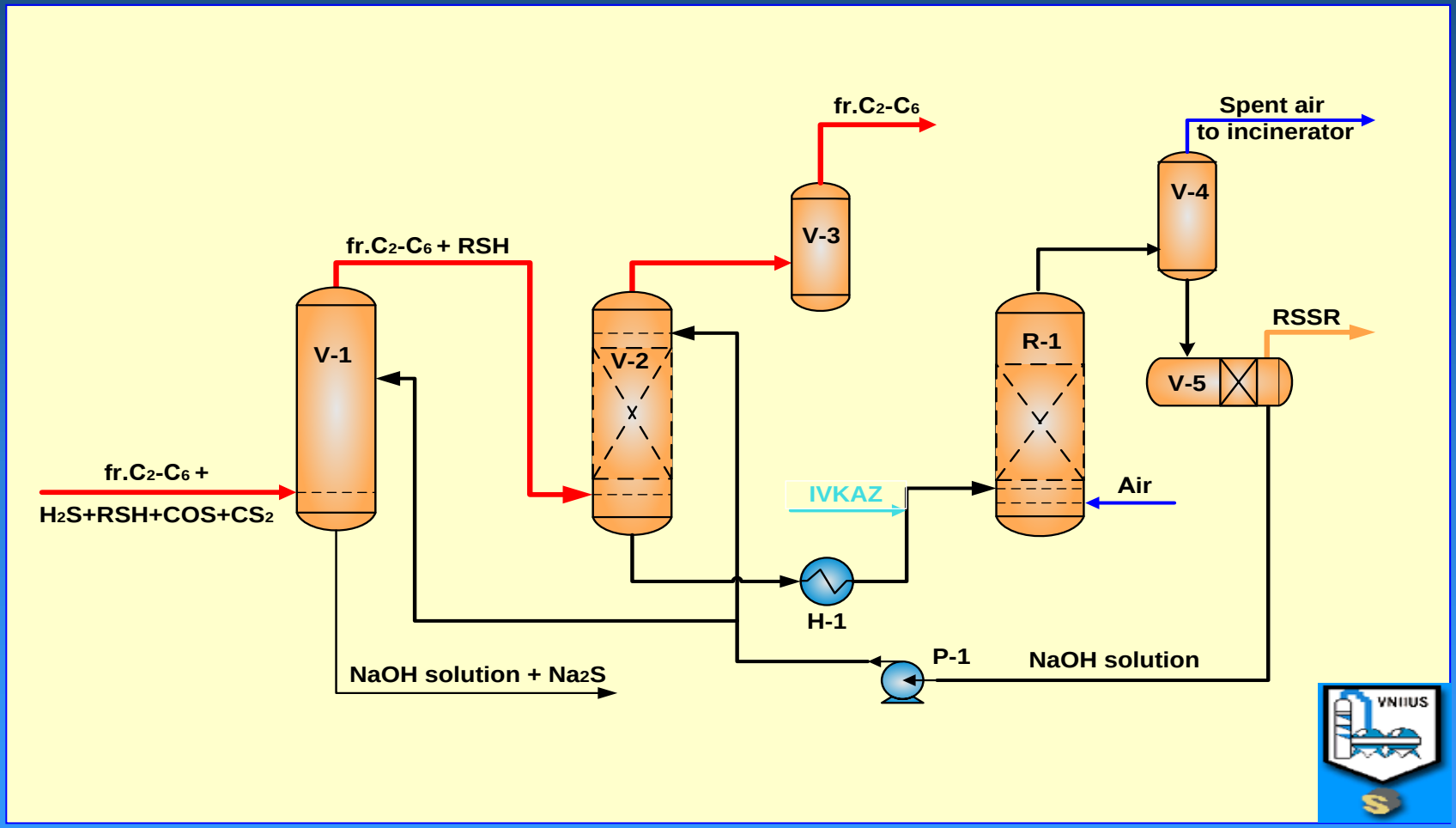
Operation conditions and consumption rates of major materials for DMC processes

Operation conditions	Approximate range
Feed capacity, bbl/day	50 000 – 300 000
Process temperature, deg.C	40 - 70
Process pressure, bar	6 - 15

Materials and utilities	Approximate consumption rates per ton of feed
Sodium hydroxide, g	40-150
IVKAZ catalyst, g	0.05-0.2
Process air, nm^3	2.0-5.0

DMD-2M PROCESS

for treatment of liquified hydrocarbon gases for hydrogen sulfide and mercaptans



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Reactions in extractor DMD-2M

$H_2S + 2\ NaOH \rightarrow Na_2S + 2\ H_2O$ (1)

$RSH + NaOH \rightarrow RSNa + H_2O$ (2)

$COS + 4\ NaOH \rightarrow Na_2S + Na_2CO_3 + 2\ H_2O$ (3)

$CS_2 + 6\ NaOH \rightarrow 2\ Na_2S + Na_2CO_3 + H_2O$ (4)

Reactions in regenerator DMD-2M

$3\ Na_2S + 4\ O_2 + H_2O \rightarrow Na_2S_2O_3 + Na_2SO_4 + 2\ NaOH$ (5)

$2\ RSNa + 0.5\ O_2 + H_2O \rightarrow RSSR + NaOH$ (6)

Advantages of DMD process

TECHNOLOGY :

- **DMD-2M process allows to treat feed for four types of sulfur compounds (H_2S + RSH + COS + CS_2). For COS and CS_2 removal a special additive in a caustic solution is used on extraction stage.**

CHEMISTRY :

- **DMD process uses highly active and stable homogeneous IVKAZ catalyst, commercial production of which is organized in Russia.**

Advantages of DMD process

ENVIRONMENT :

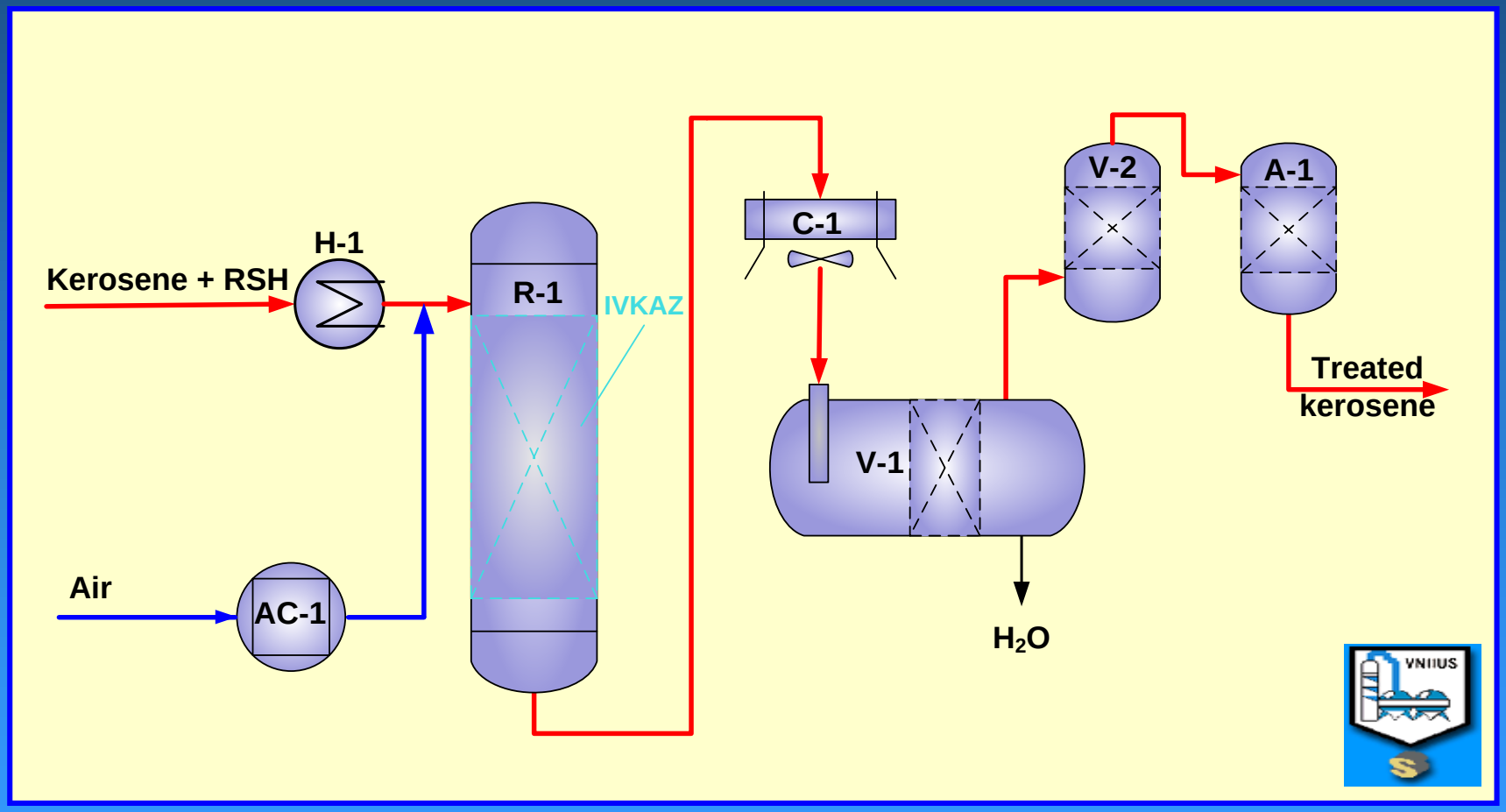
- **DMD process together with Serox unit is a complex for light hydrocarbon feed treatment for toxic sulfur compounds without producing hazardous wastes and without environmental damage.**

ECONOMY :

- **The efficiency of DMD technology is as high as that of Merox (UOP) and Sulfrex (IFP) processes.**

DMD-1 PROCESS

for demercaptanization of kerosene and diesel distillates, total sulfur content in which does not exceed a norm. DMD-1 process allows to decrease mercaptan sulfur content in kerosene below 20 ppm



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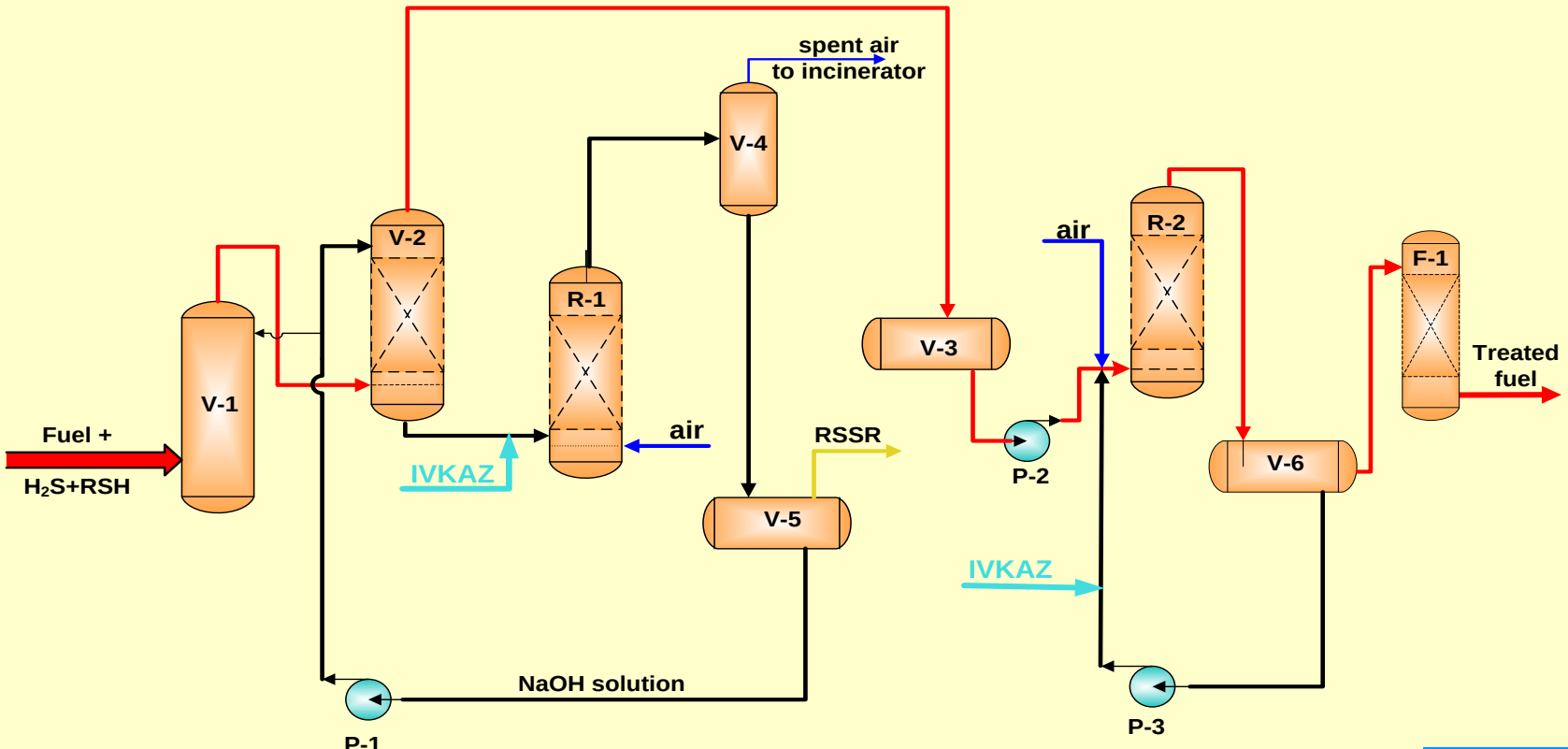
DMD-3 PROCESS

for treating straight-run gasoline fraction (62—180 °C) or catalytic cracking gasoline with high mercaptan sulfur content for hydrogen sulfide and mercaptans



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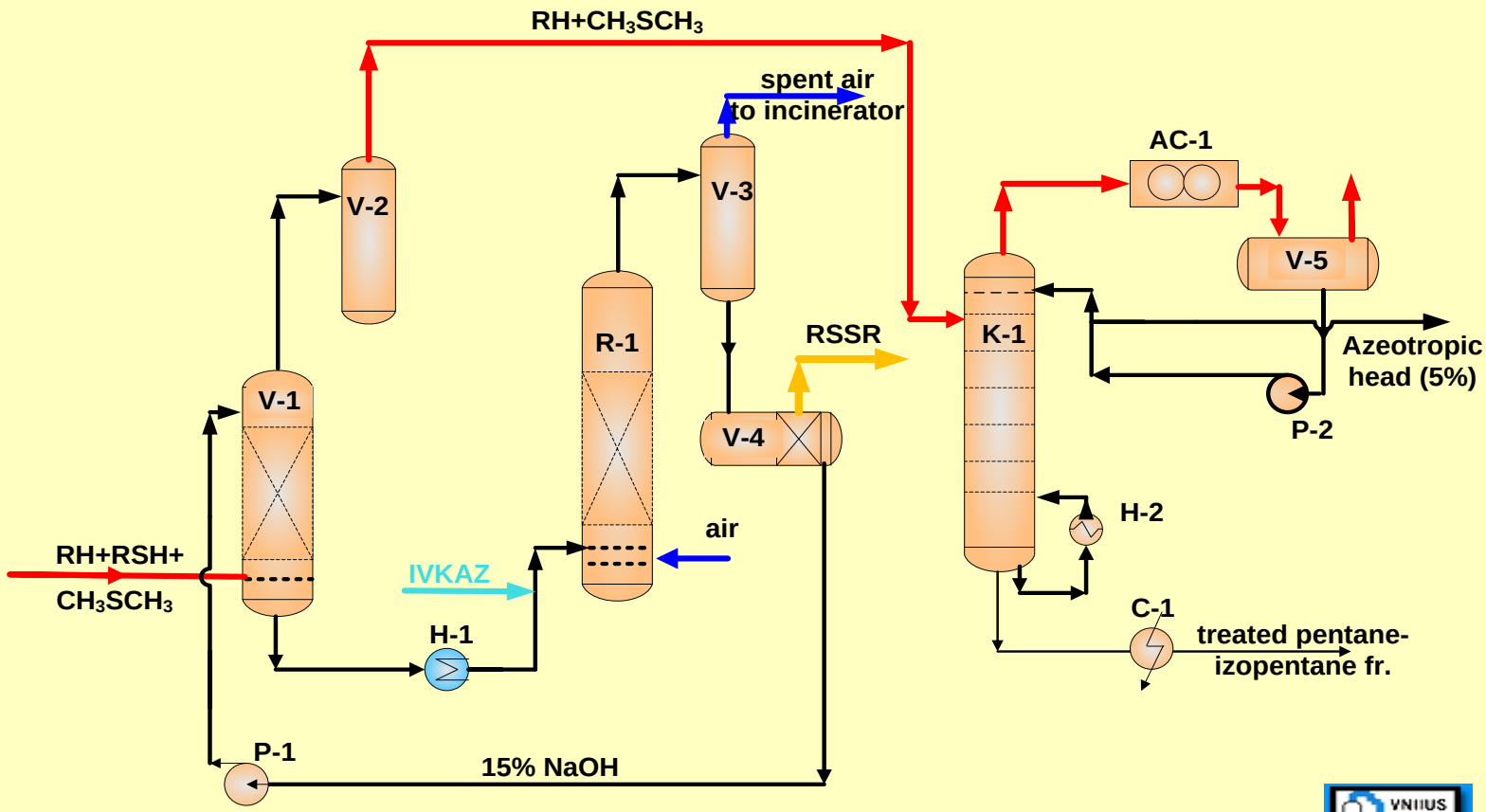
DMD-4 PROCESS

for treating pentane-hexane fraction for mercaptans and dimethyl sulfide



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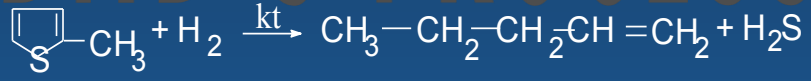
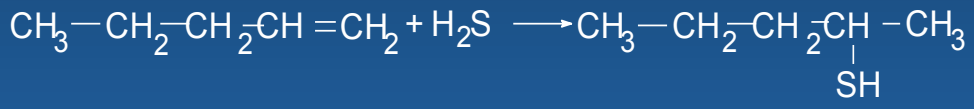
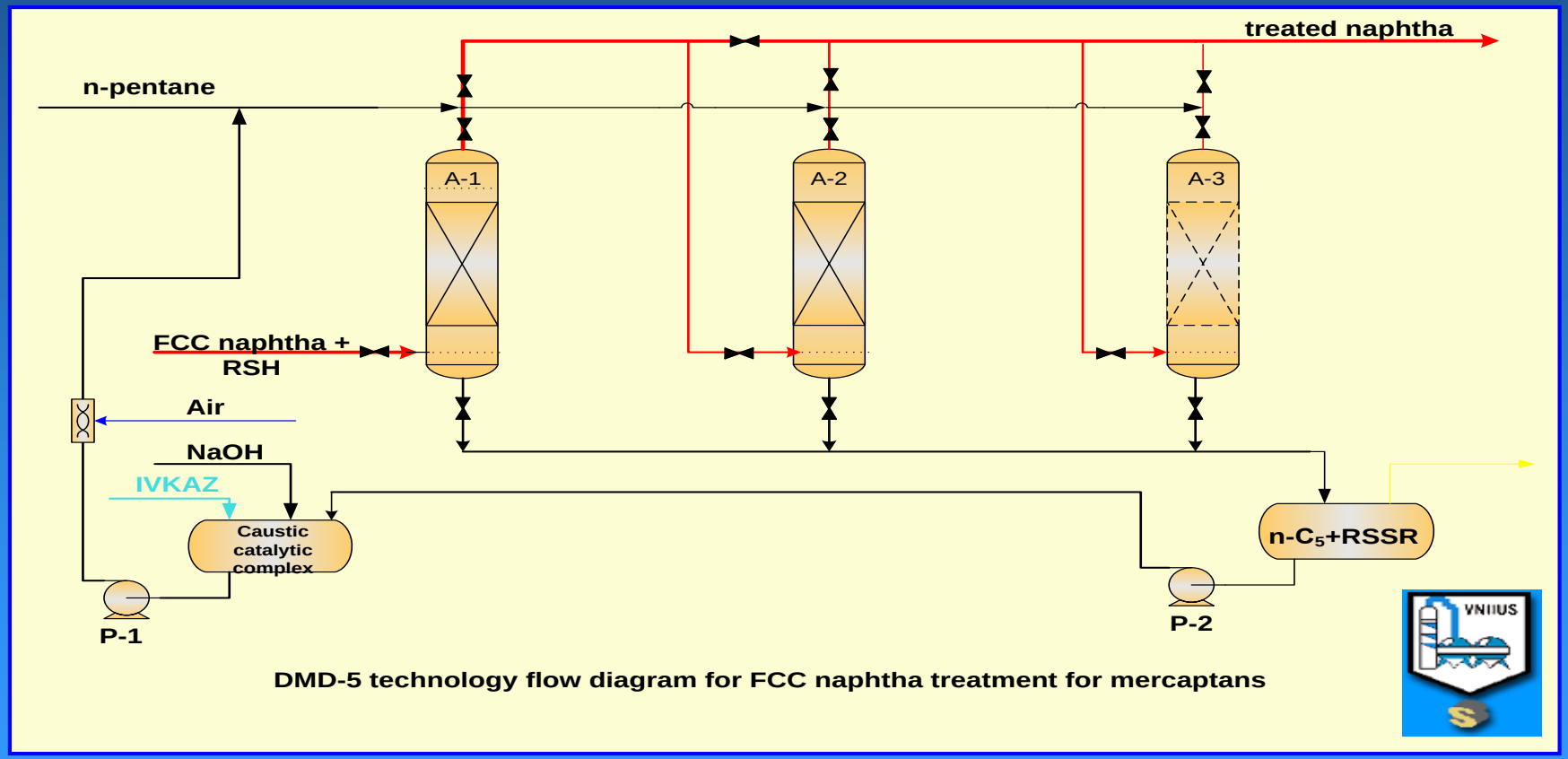
DMD-5 PROCESS

1) 

2) 



DMD-5 technology flow diagram for FCC naphtha treatment for mercaptans

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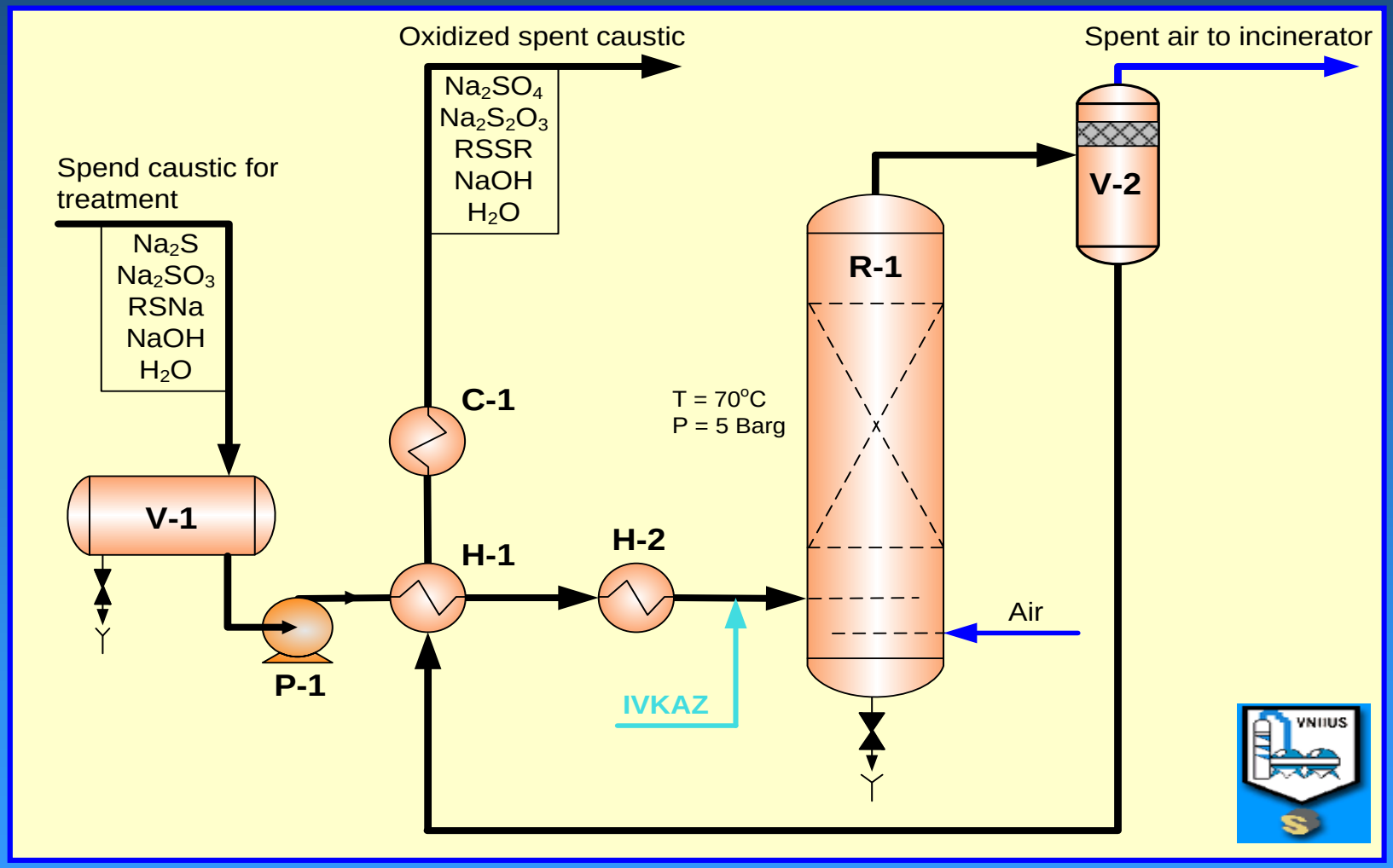
Serox-W PROCESS

for treating sulfur-alkaline waste waters and technological water condensates for sulfur compounds



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Desulfurization IVKAZ catalyst

is designed for application on plants of:

- *alkaline treatment of oil and gas condensates for hydrogen sulfide and mercaptans;*
- *alkaline treatment of liquified hydrocarbon gases for hydrogen sulfide and mercaptans;*
- *treatment of a straight-run gasoline fraction (fr.62-180oC) or catalytic cracking gasoline with high mercaptan sulfur content for hydrogen sulfide and mercaptans;*
- *treatment of sour gas condensates and light hydrocarbon fractions for hydrogen sulfide and low-molecular weight mercaptans;*
- *demercaptanization of pentane-hexane fraction;*
- *treatment of sulfur-alkaline waste waters for sulfur compounds;*
- *ammonia-catalytic treatment of heavy oils for hydrogen sulfide and mercaptans;*
- *of MEROX processes.*

JSC "IVKAZ" invites companies for cooperation in supplying IVKAZ catalyst to refineries. We are ready to consider your proposals about mutually advantageous cooperation.

Thank You
for attention !