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## **Desulphurization of Petroleum Products and Sewage Decontamination Using New Advantages of Heterogeneous Catalyst**

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### **Abstract**

**Comparative analysis of homogeneous-catalytic and heterogeneous-catalytic processes at sweetening (demercaptanization) light hydrocarbons, kerosene, gas condensates and light oils, as well as disposal of sulfur-alkaline wastes. The advantages of the proposed heterogeneous polymer-based KSM catalyst. Ways of reducing total sulfur content in light oils and gas condensates.**

**Key words: sweetening of light hydrocarbons, jet fuel, gas condensates and light oils; heterogeneous KSM catalyst; disposal of sulfur-alkaline wastes.**

### **1. Light hydrocarbons demercaptanization (sweetening)**

Light hydrocarbons purification is based on mercaptans extraction using alkaline solution with the following regeneration by oxidation of alkali mercaptides to disulfides in the presence of a catalyst:



Disulfides formed are not soluble in an alkaline solution. They are removed from the regenerated alkali by gasoline extraction.

When using homogeneous catalysts dissolved in alkaline the formation of disulfide extends beyond the regenerator – in pipelines or in the extractor. Disulfides formed are moved in an extractor from circulating alkaline solution to cleaning light hydrocarbons and therefore increasing the total sulfur content in the purified product.

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- Reduction of total sulfur in the purified product less than 10ppmw by eliminating contamination of disulfides.
- Reduce operating costs by increasing the lifetime of the alkaline solution from 3 months to 1 year and lifetime of the catalyst from 3 months to 10 years.
- Sweetening units' environmental improvements by reducing the volume of sulfur-alkaline waste, reducing the concentration of free alkali and getting an exception of heavy metals in waste water.

Thus, in BBF, sweetened from mercaptans by Demer-LUVS at JSC "TAIF-NK", mercaptan sulfur contents is 1 ÷ 5 ppmw, and total sulfur content – does not exceed 10 ppmw. Similar results were obtained in JSC "LUKOIL-NizhegorodNOS" the content of mercaptan sulfur in BF – less than 5 ppmw, and total sulfur found by the ANTEK device less than 10 ppmw.

## 2. Kerosene (jet fuel) fractions demercaptanization

With the putting into operation of hydrocracking refineries there were significant resources of desulfurized kerosene fractions. This makes it possible to increase the production of jet fuel due to the involvement of virgin kerosene fraction by manufacturing composite jet fuel TS-1 or Jet A-1. To involve the entire volume of virgin kerosene in the composite jet fuel it is needed to sweeten it from mercaptan sulfur content, which is 4 ÷ 10 times higher than normal, acceptable to jet fuel – 0.003 wt%.

In this context, becomes actual the process of selective oxidation of corrosive mercaptans into inert disulfides in alkaline medium at 40 ÷ 60°C. Estimated capital cost for hydrotreatment of kerosene compared with alkaline sweetening is higher 10 ÷ 20 times, and operating costs – 20 ÷ 50 times.

The main obstacle to widespread adoption of the known processes of alkaline kerosene sweetening using based on coal catalysts – is their multistage and ecology. The fragility of the adsorption interaction of porous carbon with an alkaline solution of ACS leads to constant erosion of the long carrier. This calls for constant feeding of coal and cleaning the fuel from the ACS, which leads to the formation of the multistage waste at all stages of jet fuel purification (Fig. 2):

- Alkaline cleaning of kerosene from acidic impurities – 18 L. Sulfur alkaline waste (SAW)/tn.
- Kerosene water flushing from blown ACS – water consumption 18 L./tn.
- Kerosene salt drying from moisture and traces of ACS – salt consumption 0.26 kg/tn.
- Bleaching clay purification from traces of ACS and resins ≈ 95 tn./year to dump.

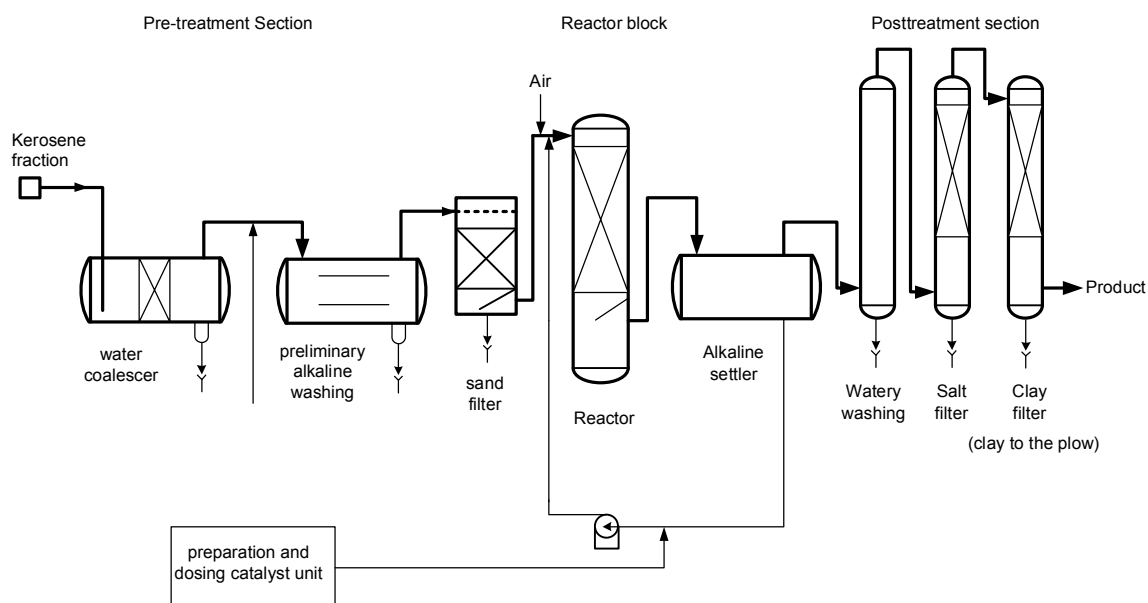


Fig. 2 Typical kerosene sweetening process using the coal based catalyst.

Instead, these processes, we propose two-stage regenerative low-waste "Demer-KSP" kerosene treatment process using polymer KSM catalyst in conjunction with the promoter that can quantitatively settle from kerosene in 60 ÷ 90 min. In this case, together with sweetening, in the same reactor promoter is extracting acidic impurities from

kerosene, as well as part of the reaction and dissolved water, which are then picked out while promoter regeneration (Fig. 3).

Significant advantages of the "Demer-KSP" process using KSM catalyst and promoter compared with listed above processes are:

- Reduction of capital and operating costs for jet fuel cleaning due to the exclusion the following units:
  - Preliminary alkaline treatment of kerosene from acidic impurities.
  - Sweetened jet fuel water washing from traces of ACS.
  - Kerosene moisture salt drying.
  - Kerosene bleaching clay adsorptional purification from traces of copper salts.
- Improving ecology of the Refinery by eliminating of alkali naphthenate toxic wastes, cobalt salts and clay slurry.

Experimental batch of virgin kerosene, sweetened by pilot plant of the Moscow Refinery using "Demer-KSP" method, has successfully passed the qualification tests in VNIINP (All-Russian Research Institute for Oil Refining). With three major Refineries in Russia concluded license agreement for the implementation of this process.

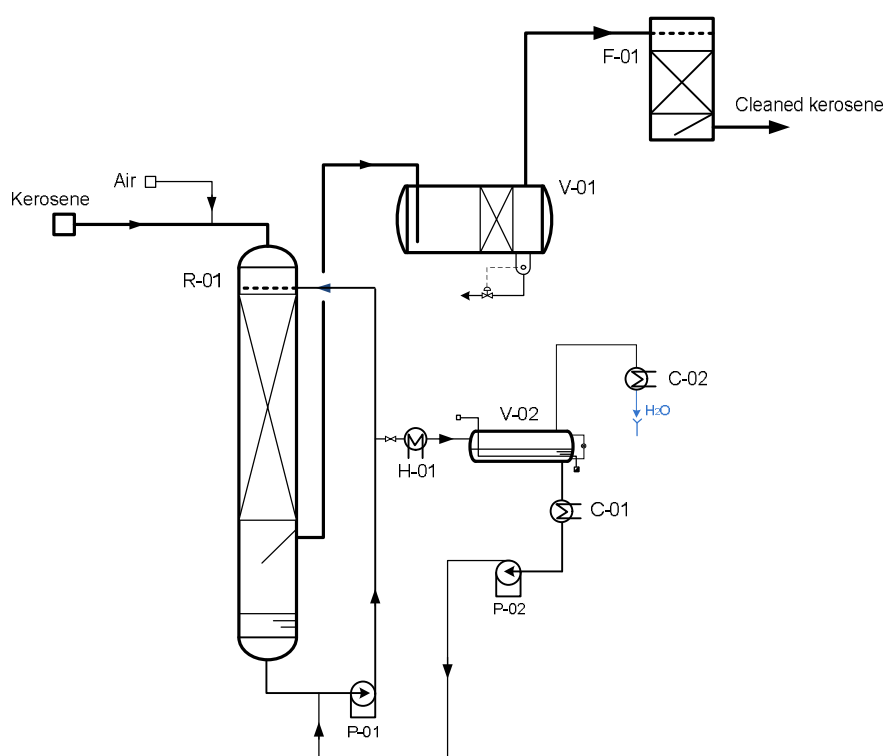


Fig. 3 Sweetening kerosene fractions using "Demer-KSP" method.

(R-01) – reactor; (V-01) – settler; (V-02) – evaporator; (P-01/02) – pumps; (H-01) – heater; (C-01/02) – cooler (F-01) – sand filter.

### 3. Demercaptanization of gas condensates and light oils

During hydrotreatment of Astrakhan high mercaptan gas condensate was established that the presence of mercaptans in the feed leads to increase the frequency of regeneration. The reason is the intensive formation of coke deposits by thermal decomposition of mercaptans with polymerization products of their decomposition on the catalyst. The share of these products up to 60% by weight of coke deposits.

These data indicate the feasibility of pre-sweetening high mercaptan raw before hydrotreatment. This scheme is attractive in terms of reducing the corrosivity of the material in case of mercaptans removal that causing intense corrosion of equipment in the heating zones due to the mercaptans low threshold of thermal stability (140 ÷ 170°C).

The share of mercaptan sulfur has a number of fields from 14 to 67% of the total sulfur content (Table 1).

Table 1. The content of total and mercaptan sulfur in the oil and gas condensate depending on the location.

Feed	[S] % wt.	[S <sub>RSH</sub> ] % wt.	[S <sub>RSH</sub> ] %relative	S <sub>CH<sub>3</sub>SH</sub> % wt.	S <sub>C<sub>2</sub>H<sub>5</sub>SH</sub> % wt.
Astrakhan condensate	1.38	0.19	13.8	0.0010	0.0160
Orenburg condensate	1.25	0.84	67.2	0.0005	0.0010
Karachaganak condensate	0.67	0.16	23.9	0.0022	0.0105
Condensate Carter Creek (USA)	0.64	0.185	28.9	0.0100	0.0200
Qatar condensate (Arabian Peninsula)	0.26	0.17	65.4	0.0017	0.0313
Oil Yamashev (Russia, RT)	3.16	0.14	4.4	0.0002	0.0068
Zhanazhol oil (Kazakhstan)	0.47	0.18	38.3	0.0012	0.0063
Novolabitskaya oil (Ulyanovsk region)	4.58	0.35	7.6	0.0025	0.0225
Markov oil (Irkutsk Oblast)	1.0	0.41	41.0	0.0035	0.0085
Duglass oil (UK)	0.40	0.13	32.5	0.00005	0.00005
Tengiz oil (Kazakhstan)	0.66	0.08	12.1	0.0150	0.0200

In nowadays processes of oxidative or extractive oil demercaptanization by ACS water-alkaline solutions is solving only the problem of deodorization by the oxidation of light C1-C2 mercaptans in oil to disulfides and to satisfy GOST R51858-2002 requirements and provide acceptable terms of its transportation in Russian Federation or abroad. Thus formed disulfides remain in the oil, i.e. sulfur content in oil is not changed (see Table 2).

Table 2. The composition of sulfur compounds in the Tengiz oil before and after purification by oxidation sweetening.

Components	T <sub>boiling</sub> , °C at 760 torr	Concentration in ppmw		Residual amount, S, % relative
		Before sweetening	After sweetening	
Hydrogen sulfide	- 60.40	1.63	0	0
Methane thiol	6.00	57.0	0.26	0.50
Ethane thiol	35.00	74.32	1.39	1.87
Iso-propane thiol	52.56	42.72	13.28	31.09
n-propane thiol	67.60	16.46	4.26	25.88
Tert-butane thiol	64.22	5.82	5.44	93.47
Secondary butane thiol	84.98	39.40	31.40	79.70
Dimethylsulfide	37.50	1.86	1.8	96.77
Methylethylsulfide	66.65	1.27	1.27	100.0
Dimethyldisulfide	109.74	21.47	33.06	153.98
Methylethyldisulfide	58(57 torr)	17.38	82.08	472.27
Diethylsulfide	154.10	2.96	26.5	895.53

Table 2 shows that the use of oil oxidation sweetening completely oxidized only methyl and ethyl mercaptans. Heavier propane thiol oxidized by 70% and butane thiol – 20%. The residual mercaptans and disulfides formed remain in the oil, causing corrosion and formation of coke deposits at subsequent high-temperature hydrotreatment processing, because disulfides also have low thermal stability and decomposing into the mercaptans and hydrogen sulfide when heated above 200°C.

To facilitate the subsequent processing of high mercaptan gas condensates and light oils we have developed "Demerus" process. The distinguishing feature of Demerus is using of special extractant capable of removing mercaptans from a high-boiling hydrocarbons. Extractant settling time from the purified gas condensate does not exceed 90 minutes. Aqueous alkaline solution under these conditions is not settled even for 300 minutes (see Table 3).

Table 3. Comparative analysis of efficiency of mercaptans extraction by Demerus extractant and aqueous-alkaline solution.

No.	Cleaning product	[S <sub>RSH</sub> ] <sub>initial</sub> % wt.	Demerus extractant		Aqueous 20% KOH	
			η <sub>extr.</sub> %	τ <sub>settle</sub> , min	η <sub>extr.</sub> %	τ <sub>settle</sub> , min
1	Orenburg gas condensate wide fraction of light hydrocarbons	0.28	97.4	1.0	45.0	3.0
2	2-methylpropanthiol in decane	0.21	99.1	0.5	97.0	1.0
3	Gasoline of Karachaganak gas condensate	0.35	94.3	7.0	37.1	20.0
4	Perm condensate	0.25	68.0	75.0	13.1	240.0*
5	Karachaganak condensate	0.23	67.4	90.0	13.0	300.0*

\*- aqueous extract in the presence of phenolphthalein is colored.

As seen from Table 3, in case of "Demerus" process gasoline fraction is extracted up to 94% out of mercaptans (and 37% with the usual alkaline extraction), from gas condensate – up to 67% of mercaptans (against 13%). By extracting mercaptans decreases the total sulfur content in the gas condensate (see Table 4).

Table 4. Treatment effect of mercaptan and total sulfur content at Orenburg gas condensate depend on technologies.

No.	Sweetening technology	S <sub>RSH</sub> initial %wt.	S <sub>RSH</sub> residual %wt. (relative)	S <sub>total</sub> initial, % wt.	S <sub>total</sub> residual, % wt. (relative)
1	Extraction by 15% watery NaOH solution	0,6	0,3 (50)	1,81	1,51 (83.4)
2	Gas condensate extraction by Demerus extractant	0,6	0,14 (23)	1,81	1,35 (74.6)
3	Demer-KSP method (τ <sub>oxidizing</sub> =120 min)	0,6	≤ 0,005 (0.8)	1,81	1,81 (100)
4	«Demerus», then Demer-KSP (τ <sub>oxidizing</sub> =60 min)	0,6	≤ 0,005 (0.8)	1,81	1,35 (74.6)

Extractant regeneration is carried out by oxidation of contained mercaptides to disulfides using KSM catalyst (Fig. 4).

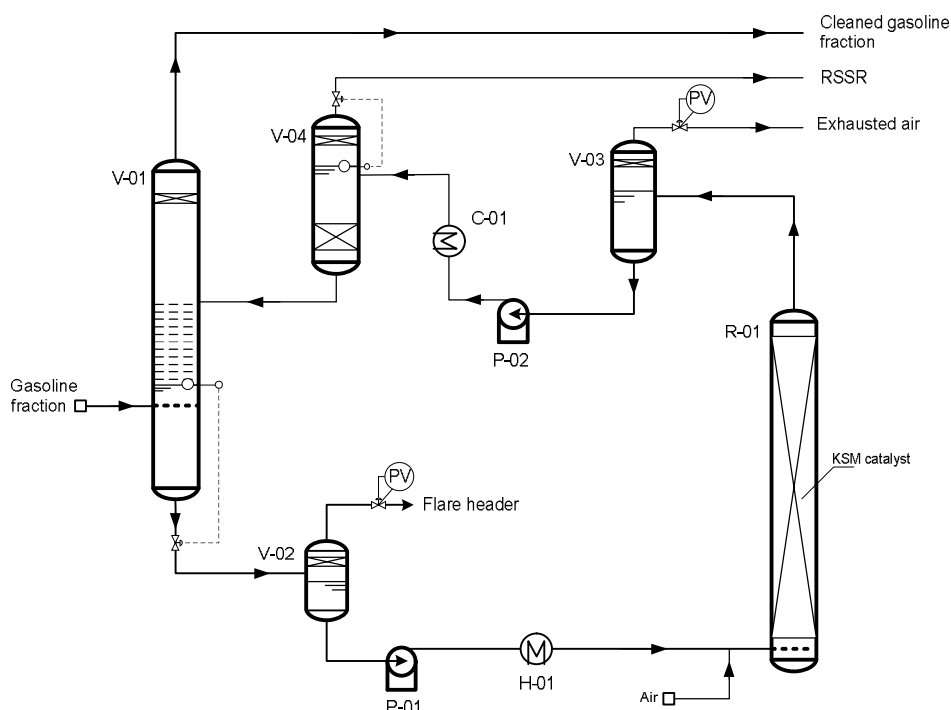


Fig. 4 "Demerus" process for sweetening gasoline fractions.

(V-01) – extractor; (V-02) – degasser; (V-03) – degasser; (V-04) – settler; (R-01) – regenerator; (P-01/02) – pumps; (H-01) – heater; (C-01) – cooler.

At the same time decided important task of obtaining by high mercaptan raw disulfide oil – a valuable petrochemical product that is an effective agent for sulfuring catalysts of hydrogenation processes and an inhibitor of coke formation during pyrolysis of hydrocarbons.

#### 4. The process of local catalytic oxidation waste decontamination – LOCOS

The essence of LOCOS process is oxidizing by atmospheric oxygen toxic sulfide contained in the wastes to less harmful oxygen-containing compounds – thiosulfate and sodium sulfate or ammonium sulfate and mercaptides – to inert disulfides and further alkylthiosulfonates by the following reactions:



Unlike the original sulfides and mercaptides formed thiosulfate, sodium sulfate and alkylthiosulfonates do not have odor and have much higher limit values for plant's biological wastewater treatment. It is easily achieved at the expense of the actual dilution of oxidized sulfur-alkaline waste with offsite runoff before it enters the biofeedback.

LOCOS process is taking place in the presence of the KSM catalyst at 70–80°C and a pressure of 0.5 MPa. After the complete oxidation of toxic sulfide and mercaptides the waste is sent to the site of neutralization before discharging it to the biofeedback (Fig. 6).

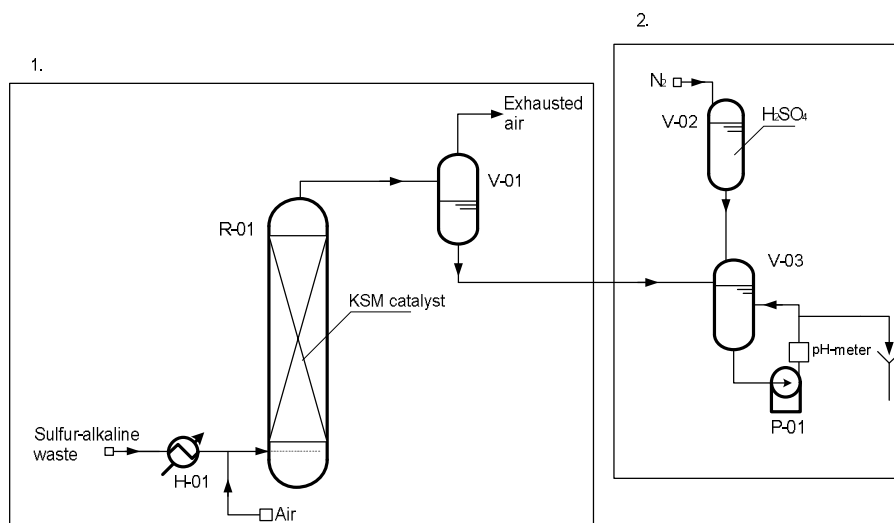


Fig. 6 Sulfur-alkaline waste water decontamination unit, where

1 – hydrogen sulphide oxidation unit,

2 – neutralization unit of oxidized wastes.

(V-01) – degasser; (V-02) – vessel for  $H_2SO_4$ ; (V-03) – neutralizing vessel; (R-01) – regenerator; (P-01) – pump; (H-01) – heater.

To reduce water consumption and to provide circulating water supply it is appropriate to provide for desalting oxidized and neutralized wastes by known methods such as reverse osmosis.

In contrast to the process of sulfur-alkaline waste water carbonization or liquid-phase oxidation method, LOCOS process does not require much heat and chemicals and does not pollute the air emissions by hydrogen sulfide or sulfur dioxide. The alkaline nature of the reaction medium and the relatively low temperature of the process allow using apparatus made of carbon steel. The use of KSM catalyst in LOCOS process can significantly increase the efficiency of sulfur-alkaline waste decontamination in comparison with carbon fiber oxidation catalyst or noncatalytic method:

- 1) Reduce the temperature and shorten the oxidation time of sulphides and mercaptides by air oxygen.
- 2) Provide a deeper oxidation of sulfur compounds and decrease chemical oxygen demand by about 75%.
- 3) Reduce the amount of toxic mercaptans in the exhaust air.

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