ATTACHMENT 2

Desulphurization Plant for Petroleum Products

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Desulphurization Plant for Petroleum Products

The problem of reducing the Sulphur content (desulphurisation) in petroleum products attracts a great deal of attention from domestic and foreign researchers.

According to numerous foreign and Russian researchers, one of the most promising methods for desulphurization of petroleum products is the oxidation of products with a mixture of ozone and air.

"The use of the proposed desulphurization technology is promising, in the first place, for mini-oil refineries that, with poor financial capacity, are unable to install expensive and energy-intensive oil refinery group. However, the possibility of scaling back the proposed technology will allow it to be used in large oil refineries, thereby improving the quality of oil and reducing the financial burden on the enterprise.

Existing Technologies

The three main methods of removing sulfur are:

1. Hydrotherapy. The method is based on the treatment of lubricating oils and liquid paraffins with hydrogen (or gas containing hydrogen), at a temperature of 200-3250 ° C, at a pressure of 4-5 MPa, in the presence of a catalyst. The gas/supply ratio is 300:1. Gas consumption - 0.2-03% of the total mass. As a result, H2S, NH3, H2O and N2 are released.

2. Hydrocracking. When using this method, the raw material is also treated with hydrogen (or gas containing hydrogen), but at a high temperature and pressure of 300-450°C and 5-30 MPa respectively, in the presence of a catalyst. Fractions of high-boiling oil are processed, mainly vacuum distilled with a boiling point of 300- 540 ° C.

3. Hydrodesulphurization. They are used to remove sulfur from the high-boiling fractions (boiling point 540-580°C) of tar, fuel oil, deasphalted oil. The process is carried out at 360 - 430°C and a pressure of 10-20 MPa, the gas-feedstock ratio (600-1000):1.

The technological schemes of the processes are very similar: heating of the components, mixing and processing in the reactor, cooling of the hydrogenated product, separation of gases containing hydrogen and hydrocarbons from it respectively in high and low pressure separators, with subsequent distillation into target products, gas purification from H2S, NH3 and H2O.
Attention is drawn to the large excess of gas and its very low use in hydrogenation reactions, typical of heterogeneous processes.

The activation of processes in all cases is signaled by heating and is enhanced by catalytic reactions. Note that the presence of sulfur, metals, aromatic hydrocarbons leads to rapid passivation of catalysts.
In these processes, hydrogenolysis reactions occur, that is, the bonds of carbon with sulfur, metals, oxygen and nitrogen are broken. Under conditions of excess hydrogen, H2S, NH3 and H2O are formed, etc.
Purification of petroleum products from sulfur is also carried out by treatment with acids, alkalis and other reagents.

Processes have many disadvantages

The disadvantages of these methods include high energy consumption, complexity of instrumentation, irrecoverable losses of expensive catalysts, system complexity and selectivity of methods in relation to the sulfur compounds removed, increased explosiveness, environmental toxicity, environmental risk, etc.
In the modern oil refining industry, under conditions of strict requirements for the quality of petroleum products and the depletion of liquid hydrocarbon reserves of "light" quality, promising and energy-efficient new systems are required, which make it possible to provide: processing of petroleum products without the use of expensive catalysts, increased processing depth of liquid petroleum products, reduction of the content of harmful impurities, improvement of the quality of the output product.
Therefore, a method for the oxidation of sulfur-containing compounds in the reaction zone with a mixture of ozone and oxygen of air is proposed.
The method is based on an important property of sulfur-containing saturated organic compounds: they oxidize much faster than hydrocarbons, which is explained by their lower thermodynamic strength. For example, for thiophene, ^H°t is 19.6 kcal/mol, while for SO2 it is 70.96 kcal/mol.

Irreversible oxidation potential

Links	Potential
nonilmercaptano	0,216
thiophene	0,342
thioxane	0,346
dibutyl sulfide	0,352
Dihexyl-sulfide	0,358
Dicycloec-sulfide	0,48
diphenyl sulfide	0,361
thiophanes	0,416
Methylteophene	0,409

Thermodynamic performance of compounds

Links	N kkal
thiophene	19г6
tetrahydrothiophene	23,5
butylmercaptan	38,48
Toluene	38,49
heptanol	48,17
Nonane	54,74
SO2	70,96
H2O	57,8
FeS	22,72

Therefore, the treatment of sulfur-containing petroleum products with a dosed dose of an ozone-air mixture ensures the complete removal of sulfur itself, without affecting, in practice, other hydrocarbons. This circumstance allows its application in technologies for the processing of petroleum products.

The main advantage that attracts the attention of both domestic and foreign scientists is the possibility, with a fairly simple design, to carry out the processes of mixing, dispersion and activation of liquid substances, creating a significant energy density per working volume group.

The use of our method allows the complete removal of sulfur and sulfur compounds in petroleum products.

The quality of the crude oil desulphurization process in an electromechanical converter with a discrete secondary part was determined by sampling the oil that had been processed in the device every 10 seconds. To find the optimal processing parameters (time) during the desulphurization process, dependencies on the amount of sulfur removed from the processing time were obtained.

The quantitative Sulphur content of petroleum products was determined by energy- dispersive X-ray fluorescence spectrometry.

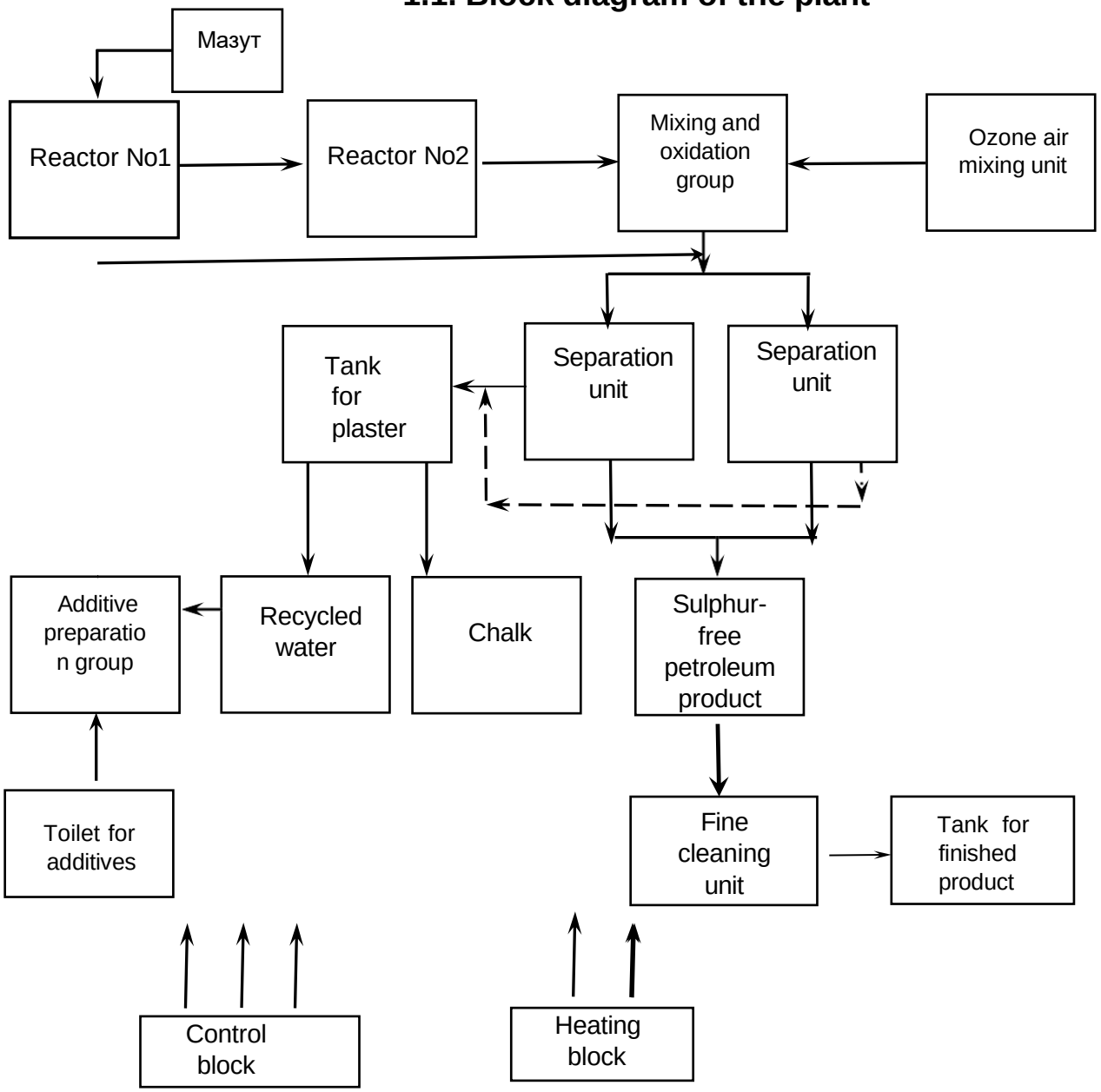
The range of variation in desulphurization efficiency in the experiments was up to 97 %, depending on the processing time.

Based on the effectiveness of the presented technological process, we proposed options for the implementation of technology in production facilities. The PSAF-4 installation was developed and tested.

GENERAL INFORMATION ABOUT THE INSTALLATION "PASF-4/5" AND ITS PURPOSE

The PASF-4/5 Group is designed to remove sulfur, mechanical impurities and water from petroleum products

1.1. Block diagram of the plant



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Installation is a set of blocks, each of which performs a specific function.

- - Raw material preparation team, (Reactor No. 1, Reactor No. 2)
- - Oxidation group of the raw material
- - Separation group,
- - Additive preparation group,
- - blocking of separation and removal of sulfur
- - Fine purification group from impurities, sulfur residues
- - blocking automation and control

Technical characteristics of the plant "PASF-4/5"

Technical data and characteristics of the system

The working pressure of the installation is not more than - 0.6 MPa.
The continuous operating time of the filter is 24 hours.
A feature of the design of PASF-4/5 filters is the presence of an automatic regeneration system. The inner blocks are made of stainless steel.

Main technical characteristics

The main technical characteristics of the filter are presented in Table No. 1 below;

Table 1

No	Technical Specifications	Value
	Parameters of the filtered liquid	
1	Type of liquid to be purified	petroleum product
2	Viscosity of the liquid (at 1000°C), cSt	50
3	Productivity m3/hour no more	
4	Sulphur residue in dark oil products, not more than %	0.5
5	Fluid operating temperature range, °C	50 - 60
6	Diameter of the connecting pipes at the filter inlet and outlet, mm	57
7	Sediment drain pipe diameter, mm	57
8	The area for installation does not exceed sq. M.	150
9	Mounting weight, not exceeding, kg exceeding, kg	10000
10	Dispenser for special additives, not exceeding kg/hour	120
11	Climate version according to GOST 15150-69	Yes
12	Technological emissions	According to PDK

Composition of the installation and delivery set.

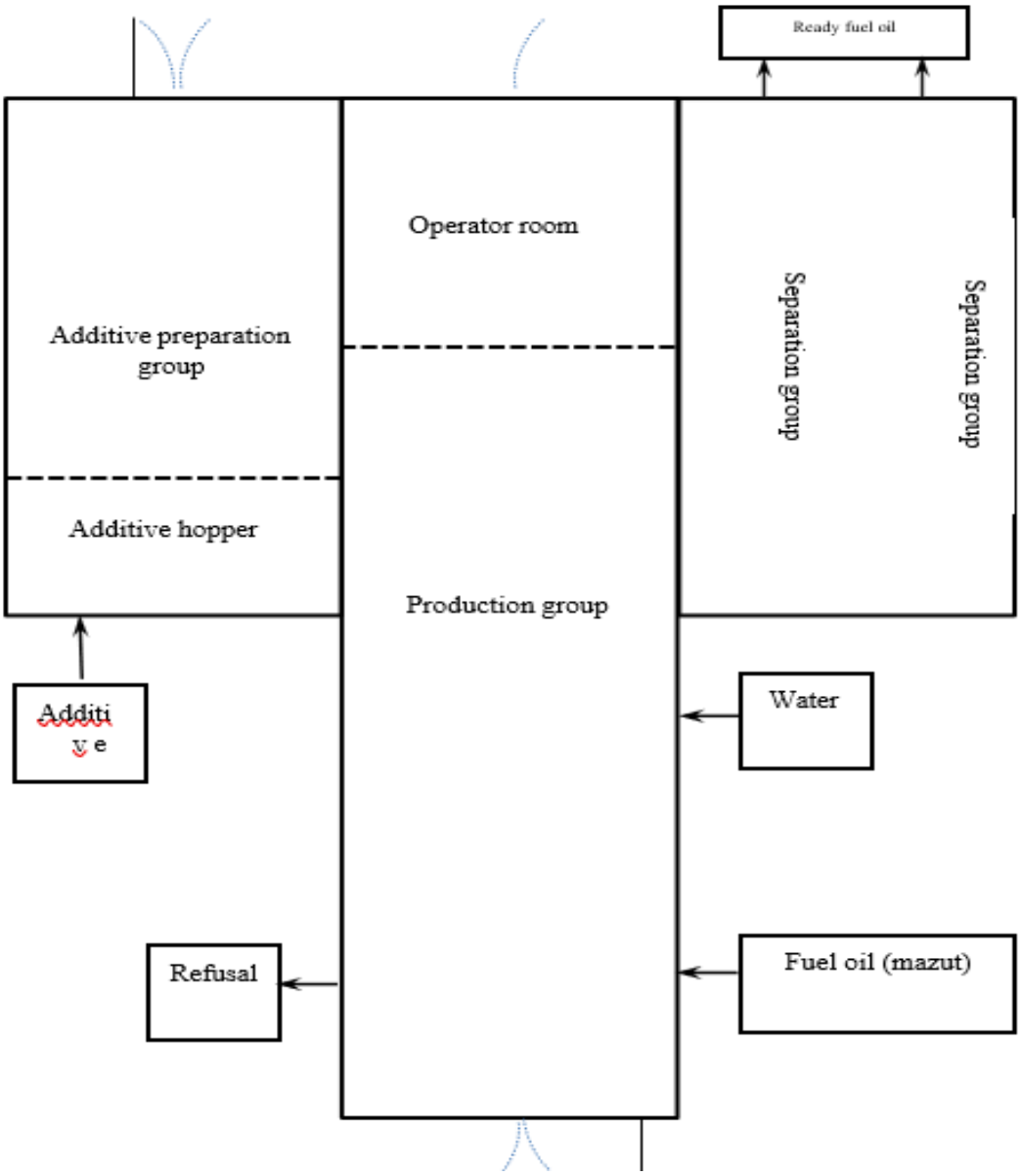
The composition of the installation is given in Table 2 below:

Table 2.

No	Parameter	Quantity
1	PASF-4/5	1 pcs.
2	Automation Kits	1 pcs.
3	Spare parts kit	1 pcs.
4	Passport and operating manual	1 pcs.
5	Installation Certificate	1 pcs.

PASF Installation Block Placement Scheme-4 /5

Block for the automatic preparation of additives with a hopper, a auger for automated powder feeding for additive production. Additive preparation tank, metered water supply tank for additive manufacturing, finished additive receiving tank and related supply to the system.



The dimensions of the "Fluff Preparation Block" and the "Separation Block" are 6000x2450x2450mm

The dimensions of the "Production Block" including the "Operator" are 12000x2450x2450mm

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Scheme of operation of the plant for the removal of sulfur PASF-4/5. Brief description

The PASF-4/5 installation can accept fuel oil from both stationary tanks and tankers. The temperature of the incoming product (fuel oil) must be at least 50 degrees. The temperature is automatically measured in the suction pipe when the oily product enters the Group with the help of a pump.

If the temperature is below 50 degrees, the Group does not turn on and the fuel oil supply stops. The pump will work in a reverse cycle.

If the temperature corresponds to the technological one, the Group comes into operation. At the entrance, the petroleum product, together with the air of the compressor, enters Reactor 1, Reactor 2 and then the Mixing and Oxidation Group with an ozone-air mixture. In addition, the petroleum product is separated from the air and sulfur in the "Separation Group". The petroleum product enters the "Separator 1" and "Separator 2", where sulfur compounds interact with the additive. The resulting gypsum sinks to the bottom, and the petroleum product rises upwards due to the different densities.

The gypsum from "Separator 1" and "Separator 2" is discharged via a pump into the gypsum collection hopper. The processed petroleum product enters the Fine Purification Group and from there to the Finished Product Group.

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