

Waste refrigerant fluid of the process of n-butane dehydrogenation as a source of new commercial products: resource-ecological aspect

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Abstract: The article deals with the technology of disposal of waste refrigerant fluid for the process of one-stage dehydrogenation of n-butane by oxidative thermal destruction with the production of bituminous varnish as a commercial product, which allows solving the problems of neutralizing and processing the waste of petrochemical industries and bottoms with the aim of saving resources and raw materials.

1. Introduction

The analysis of the prospects for the development of world oil and gas chemistry and oil refining shows a significant shift in priority problems towards a comprehensive assessment of the environmental friendliness and enterprises safety as well as possible consequences of their impact on the environment, life and health of the population. The objects of oil and gas processing, like many enterprises of other industries, are sources of the inevitable, potential, until now practically quantitatively negligible risk to the population and the environment. The fact should be noted, that on the one hand, oil refineries are the main driving factor in the development of all branches of industry, transport, municipal engineering and agriculture, the basis for raising labor productivity and the human wellbeing. On the other hand, there is an indisputable fact that the environmental friendliness and safety of enterprises are on the forefront of the development of the Russian Federation. Environmental friendliness and safety of enterprises are directly linked to the solution of the problem of waste disposal. Let us reveal some key points.

First, the problem of waste becomes extremely acute due to the depletion of natural resources, degradation of terrestrial ecosystems, deterioration of the quality of the natural environment caused by the growth of the anthropogenic load on the nature, including waste from the oil and gas industry. Secondly, the colossal amount of waste from the oil and gas industry and the related flow of man-made substances into the environment lead to the formation of new geological, biological and geochemical parameters of the environment, creating a threat to life on the Earth. Thirdly, the problem of disposal of oil and gas waste is reflected in normative documents of federal and regional significance. So in the decree of the Government of the Tyumen Region on the management of production and consumption wastes for the period up to 2020 (the regional target investment program), priorities are noted for reducing the negative impact of production waste on the environment, public health and innovative methods of waste processing.

Of course, an aggravation of the problem of waste became one of the consequences of the rapid development of industry, the scientific and technological revolution. Scientists, sociologists and



environmentalists derived a direct relationship between welfare growth and a decrease in the amount of waste from the population and industry [1]. Waste is something that cannot be used in this production. Waste volumes are determined based on this level of technology development. If initially the problem solution was seen primarily in the destruction of wastes – landfill, dumping into the seas and oceans and incineration, then with increasing environmental pollution, other, environmentally more acceptable measures for eliminating waste came to the fore – sorting and reusing, that is, resources recycling.

In the world production it must be strived for a situation that takes place in the biosphere: a complete recycling of matter – the secondary use of all atoms. The implementation of recycling with minimal costs (energy and others) is a grandiose technical task which requires changing all equipment and technology. At present, using up-to-date equipment and technologies, less than 10% of raw materials from the earth's interior and from the surface of the planet are converted into finished products, and 90% goes to wastes which pollute the biosphere. Large-scale technological researches and development carried out in developed countries are associated with a reorientation to a waste-free lifestyle or products yielding a minimum of waste, developing methods for waste collecting and sorting which ensure the economic efficiency of their recycling.

Non-waste production can be characterized in every possible way by the disposal of wastes generated in direct technological processes. Let us note also that fact, that non-waste technology is a priority of a new direction in a science – "green chemistry".

Analysis of domestic and foreign materials shows that non-waste technology as an element and component of green chemistry can develop in four main directions: the creation of various types of wastewater free technological systems based on existing, implemented and promising methods of purification; development and implementation of a system of modern methods for processing industrial and consumer waste; organization of fundamentally new processes for obtaining traditional types of products allowing to exclude waste; development and creation of territorial industrial complexes with a closed structure of material flows of raw materials and wastes within this complexes, having a minimum of emissions.

The content analysis of author's scientific research, monographic and patent papers showed that practically all types of production and consumption waste can be used in the national economy as a secondary raw material for obtaining many types of technical and consumer goods. The reality and technical feasibility of using wastes was proved, for example, by the practice of many domestic enterprises of various industries. What is the problem of the waste neutralizing of petrochemical industries and bottoms? Solid waste from petrochemical enterprises includes a variety of substances of organic origin. During mechanical treatment of industrial wastewater slurries and pasty precipitates are formed, which must be treated for disposal or abandonment. Dehydrogenated sludge and slurries, depending on their composition, are used in industry for a limited amount, and in most cases, they are exported to the dump. When toxic substances get into the sediments, they are subjected to thermal neutralization or disposal [2]. Bottoms and various substandard liquid products are liquid waste, in addition to wastewater. Bottoms are liquid products formed in technological processes during evaporation, extraction, rectification and filtration. Their use is practically impossible because of the high content of toxic organic and mineral substances. For this purpose, they must be neutralized.

2. Research

For the correct choice of the neutralization method, the physical and chemical properties of the components of their composition are taken into account.

These mentioned wastes cannot be neutralized by mechanical or chemical methods because of the complex composition and variety of chemicals belonging to different classes of compounds. Thermal methods for neutralizing bottoms are the most common in our country and abroad. They are selected depending on the required energy resources (steam, fuel, compressed air or electricity) and catalyzers.

In the one-stage dehydrogenation of n-butane, the cooling of the contact gas is carried out by the so-called circulating refrigerant oil. According to the design documentation, a high-boiling mixture of

aromatic hydrocarbons C₉–C₁₅ should be used as the refrigerant oil. But, due to the shortage and high cost of this fraction, a fraction of diesel fuel is currently used as the circulating refrigerant oil for cooling the contact gas of n-butane, butenes and isoamylenes dehydrogenation. In the work process, this fraction is saturated with resins, aromatic hydrocarbons and products of partial cracking of hydrocarbons, while losing its properties. In this regard, periodically part of the waste fraction is withdrawn from the system with replacement by a fresh fraction. The waste refrigerant oil taken out of the system is shipped to consumers as fuel oil (mazut) for boiler plants.

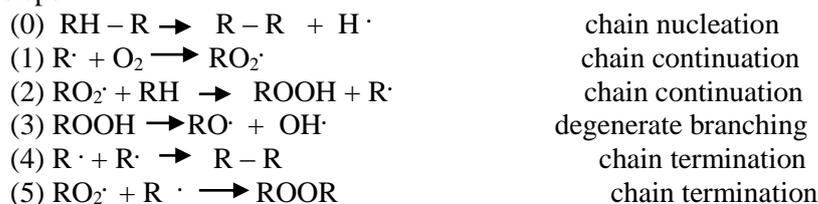
This production waste is a dark, high-solidified liquid having a density from 0.98 to 1.10 g/cm³, a viscosity above 250 mm²/s and a flash point above 80 °C.

From the standpoint of saving raw materials, energy and resource saving, a technology for the qualified salvaging of this by-product was developed. Physicochemical analysis showed that the waste refrigerating oil is identical to the high-boiling bottoms of oil refining, for example, fuel oil. Therefore, the optimal method of processing this waste is one of oxidative destruction and the production of bitumen and further the bituminous varnish on its basis.

3. Results and discussion

Let us reveal the features of the experimental part. The chemical experiment was carried out in several stages. The objective of the first stage of the experiment was the production of bituminous resin. Experiments on obtaining bituminous resin by oxidative thermal destruction were carried out in a flask with a reflux refrigerant condenser and air supply under a bed of raw materials (bubbling). The process temperature was set at 250 to 300 °C. The reaction time was controlled by the selection of the product with the determination of its properties. The yield of bituminous resin was 50% pts. wt., under optimal process conditions (reaction time 4 hours, temperature 280 °C, air consumption 2 l/min for 300 cm³ of the loaded refrigerant oil). Bituminous resin meets the requirements of GOST 21822 - 76 (grade B), namely: appearance of the film; softening point for the ring and the ball, °C; depth of penetration of the needle at 25 °C, 0.1 mm; mass fraction of substances insoluble in toluene,%; flash point, °C; solubility in linseed oil. Prior to all determinations, a sample of bituminous resin in an amount of 1 kg was dehydrated and freed from mechanical impurities. For dehydration, samples were heated for 30 minutes in a drying oven at a temperature of no higher than 180 °C and periodically stirred. The samples were heated to 60 °C and passed through a funnel with a layer of freshly calcined sodium chloride. To remove mechanical impurities, the dehydrated resin was passed through a metal sieve with a No. 07 mesh (GOST 6613-53). By chemical composition, bituminous varnish resin is a high-molecular organic compound obtained as a result of polymerization and polycondensation reactions in the presence of air oxygen of aromatic, paraffin-naphthenic hydrocarbons, resins and asphaltenes.

The mechanism of transformations is radical chain polymerization, the initiator of transformations is molecular oxygen. In the initial period of the polymerization reaction, free radicals are formed when the initial hydrocarbon reacts with the oxygen dissolved in it. The formed radical attaches an oxygen molecule to itself and is converted to a peroxide radical (RO₂·), which then breaks the hydrogen atom from the hydrocarbon molecule and forms a hydroperoxide and a new free radical (R·) which ensures the further growth of the chain. The general scheme of the radical-chain mechanism includes five basic steps.



The chain is broken as a result of recombination of radicals. In the process of oxidation, hydroperoxide accumulates, the molecules of which decompose relatively slowly into radicals. This leads to an increase in the rate of formation of free radicals [3].

As part of our study, bituminous resin performs a dual role. On the one hand, this is the final product, in demand in the fuel and energy industries and construction, and on the other hand, we regard bituminous resin as an intermediate raw material for the production of a new product - bituminous varnish. In the course of the experiment, a yield of condensate was 50%.

Therefore, the main task of the second stage was the development of a technological chain for the production of bituminous varnish. The composition of the technological chain of production of bituminous varnish includes the following stages: synthesis and study of the parameters of bituminous varnish resin, mixing of varnish resin with solvent, filtration of varnish. The properties of the oxidized product obtained were compared with the requirements of GOST for bituminous varnish (bituminous varnish BT-577 GOST 5631-79). The physicochemical properties of the initial materials and the products obtained are shown in Table 1.

Table 1. Characteristics of raw materials, substances and manufacturing products.

Product	GOST technical conditions	or	Quality indicators	Norm	Application area
1. Waste refrigerant oil (raw material)	According to the production procedure	to the	1. $\rho_{4^{20}}$ 2. Viscosity, mm ² /s	≥ 1.05 ≥ 250	Raw materials
2. Varnish resin (product)	According to the project		Softening temperature	≥ 100 °C	Intermediate raw materials
3. Solvent: oil xylene, white spirit (reagents)	GOST 14710-78 GOST 3134-78		– –	– –	Thinner for varnish
4. Light hydrocarbons (condensate, product)	According to the project		1. Density, g/cm ³ 2. Initial boiling point °C 3. T.c. End boiling point °C 4. Flash point °C	0.850...0.950 ≥ 100 ≤ 250 ≥ 30	Component of gasoline, diesel fuel
5. Siccative (reagent)	Technical conditions 20511.559-84	TU	–	–	Film drying catalyzer
6. Bituminous varnish (received commodity product)	GOST 5631-79		1. Appearance 2. Conditional viscosity, 3. The mass proportion of non-volatile substances 4. Drying time of degree 3, h.	Black liquid 18-35 37 24	Finished product

The main objective of the third stage was the development of methods, preparation formulas, research of the commodity characteristics of bituminous varnish. The composition of the formulation of bituminous varnish, obtained by a periodic method, was: varnish resin - 50%; solvent (xylene, white spirit) - 45%; siccative - 5%.

The following indicators of commercial bituminous varnish were obtained: drying time of one layer at 20 °C, - 24 hours; conditional viscosity by viscometer VZ-4 at 20 °C, - 38 seconds; mass

fraction of non-volatile substances - 37%; adhesion strength with metal - 0.2 MPa; elasticity of the film in bending, 0.9 mm; stability of the film with a static effect of water - 48 hours.

The main objective of the fourth stage of the experiment was to study the chemical composition of distillate-condensate. On the basis of the "Crystal 5000" chromatograph, after purification from unwanted components and mixing with useful additives, it was shown that in accordance with ASTM D 6729 (the "Chromatec DHA" software application), the obtained distillation condensate is a mixture of light hydrocarbons with a boiling point in the range from 100 to 250 °C; density of 0.850-0.950 g/cm³.

At the same time, the content of unsaturated hydrocarbons was no more than 2%. Oxygen-containing compounds (methanol, ethanol, tert-butanol, MTBE, ETBE, TAME) were not determined in the obtained distillate-condensate, which is the key task of the next stage of the experiment. The chromatographic analysis data allow us to state that the chemical composition of distillate-condensate can be used as a component of gasoline (gasoline fraction NK-150 °C), diesel fuel. A high octane number is provided by the presence of oxygenates - hydrocarbon oxidation products.

Based on the developed methodology, we proposed a basic process flow diagram. We will reveal the features of the process of obtaining bituminous varnish (Figure 1).

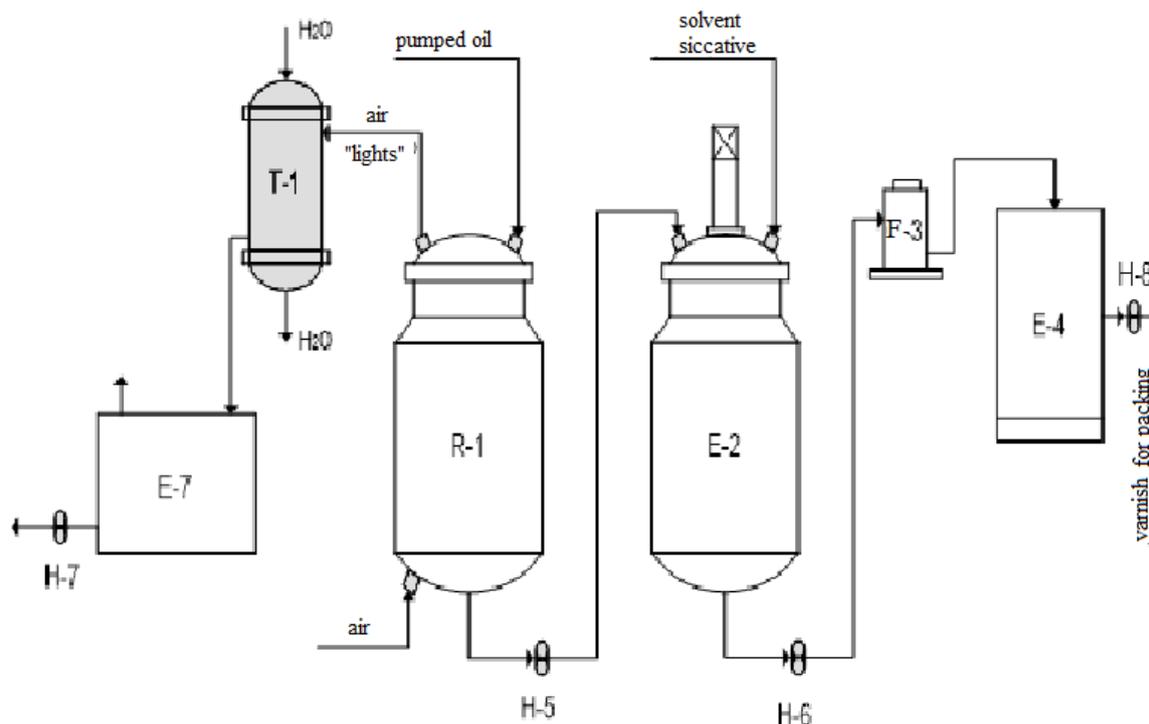


Figure 1. Principal technological workflow of production of bituminous varnish in a periodic way: T1 - heat exchanger; R1 - reactor; E2 - stirring capacity; F3 - filter "Kuno"; E4 - capacity for finished products; H5, H6, H7, H8 - pumps; E7 - capacity for collecting "light" hydrocarbons.

The waste refrigerant oil is loaded into the reactor. In the reactor, the raw material is heated and its oxidation takes place. The reaction is intensified by introducing air (up to 1500 m³/h). A sample of the oxidized product is taken through the side of the reactor to determine the softening point. The liquid varnish resin is cooled to a temperature of 130 °C and pumped to a mixer in a pump, after which the mixer is purged with nitrogen. The solvent is poured through the counter-dispenser into the reactor and is pumped into a mixer in which the varnish resin is mixed with the remaining solvent and siccative. The obtained varnish is supplied by the pump for filtration into the cartridge filter, from which the varnish flows by gravity into the capacity of the finished product. Light hydrocarbons, which escape during oxidation through the top of the reactor, condense in the refrigerant condenser and are

withdrawn for salvaging as part of light gasoline fractions. The principle technological scheme of production of bituminous varnish in a periodic way does not require expensive equipment, which is shown in Figure 1.

4. Conclusion

Thus, the raw material is a waste of the dehydrogenation process, a source of new commodity products which are in high demand in construction and engineering. Commodity qualities of the products obtained correspond to GOST and TU. It solves the problem of saving raw materials as well as energy and resource saving.

The ecological effect is related to the improvement of the ecological situation in the cities of the Tyumen Oblast on the basis of the international obligations of the Russian Federation and the environmental priorities of the Tyumen region. Utilization of heavy oil fractions will not lead to additional adverse effects and will ensure the use of new, modern technologies approved on an industrial scale. Indicators of priority of utilization of heavy oil fractions are: national (covers the territory of the Tyumen Oblast as a subject of the Russian Federation) and local (covers the enterprises of the Tobolsk industrial site).

The economic effect is obvious. Here it is appropriate to quote the words of the great scientist, our fellow countryman D.I. Mendeleev, that "burning oil is tantamount to burning accounts". The raw material effect is related to the possible use of waste as a secondary raw material for the production of bituminous resin and varnish.

The implementation of the proposed methods and technologies for the production of bituminous varnish will allow diversifying traditional production facilities, bringing them to new markets, ensuring the loading of existing production capacities, stable employment and income of the residents of the region working at these enterprises.

References

- [1] Egorov A N 2016 Waste from oil and gas chemistry enterprises *Rational Ways of Recycling. Energy Saving and Innovative Technologies in the Fuel and Energy Complex Proc. of the Int. Sc.-Pr. Conf. of Students, Graduate Students, Young Scientists and Specialists* (Tyumen) **2** pp 265-8
- [2] Egorov A N 2016 *Oil and gas processing industries. Technology. Security. Ecological compatibility* (Tyumen: IUT) p 150
- [3] Egorova G I 2017 The spent cooling liquid of the n-butane dehydrogenation process is a source of new marketable products. Resource and ecological aspect. Status, trends and problems of development of oil and gas potential of Western Siberia *Mater. of the Int. Conf.* ed Grachev S I (Tyumen: IUT) pp 94 -106