Environmental aspects of technology and technical support of PVC production based on clustering of the economy

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Abstract. The production of polyvinyl chloride (PVC) is a very promising and dynamically growing segment of the chemical industry. In the article it's considered new aspects of technical equipment of the PVC production enterprise from the point of view of reducing the environmental load on the environment. There are identified ways to reduce energy intensity and capital intensity of this production process due to the use of innovative technologies, in particular plasma-chemical pyrolysis of coke or methane contained in coke gas. The PVC production will require the development of cooperative ties between the coke chemical enterprise and chemical enterprises of the Kemerovo region on the basis of clustering of the regional economy. In the article, on the basis of data on similar enterprises, the cost of technological equipment was calculated, unit costs per unit of production and the cost of the project to create PVC production based on the raw materials of «KOKS» PJSC were determined. The use of the proposed technology will reduce the burden on the ecology of the region.

1 Introduction

At the end of 2020, the total production of unmixed polyvinyl chloride (PVC) amounted to 976.5 thousand tons, which is 0.2% more than in 2019 [1].

This sector of the chemical industry is dynamically developing, oriented to the needs of the market in this product, as indicated by the stability of the market even in the context of the pandemic of last year. The implementation of PVC production projects requires large investments, the availability of a raw material base, the creation of clusters, including enterprises of different industries, for the implementation of such enterprises.

The PVC production is a rather complex technological process, requiring complex equipment for its implementation, high energy costs, it has a negative impact on the environment. The main tasks in the production of this product are reducing energy costs; selection of the best technology to reduce investment in production capacity, especially at the semi-finished and monomer stages; reducing the environmental burden on the environment; the active use of sufficiently low-cost raw materials, which are desirably wastes of the main production or associated products obtained in the main production.

2 Materials and methods

One of the areas of solving the problem of increasing PVC production on the basis of carbon technologies is the use of non-grade coke, coke gas and methane produced from coal seams [2]. From this point of view the most rational solution is the formation of cooperative ties based on the interaction of coal enterprises and enterprises of the metallurgical industry, in particular, coke and chemical production, or the creation of a chemical and metallurgical cluster, including coke and chemical production, allowing the production of monomer and polymer. Taking into account these features, the authors tried to form production stages and evaluate the equipment of these processes, economic costs and environmental burden on the environment.

For the production of acetylene, a protruding raw material in the production of vinyl chloride by the carboxylic method, the starting material is non-grade coke, which is converted into acetylene using plasma chemical pyrolysis, which occurs in a turbulized jet of hydrogen plasma. Preliminary turbulization of plasma jet allows improving mixing of raw materials with energy carrier - plasma. Previously, coke is milled in a disintegrating machine with dimensions of 50-100 μm [3, 4]. For this ball or roll disintegrating machines are used, for example, LOESCHE, worth about 500,000 rubles up to $150,000 with a drive power of 90 to 2400 kW, depending on the performance [5]. Crushed coke is carried away from the disintegrating machine by air through a transport pipeline to cyclone dust collectors, where it is deposited and discharged through a gate to a receiving bin for supply to a plasma-chemical pyrolysis unit, and spent and dusted air is returned to the disintegrating machine. Part of the air from the closed recirculation of the pneumatic conveying system is discharged through the filter to the atmosphere. At the same time, from the point of view of ecology, it is necessary to equip the plant with sufficiently productive filters that provide high air purification.

An analysis of the technologies for the production of acetylene from coal, coke and methane showed that the most appropriate, in terms of hardware design, production costs and environmental impact, is plasma chemical pyrolysis technology.

The plasma-chemical pyrolysis plant is an object with a sufficiently high consumption of electricity (the capacity of the plant with a capacity of 136 thousand tons/year is 1.2 MW), while the conversion of coal to acetylene, using this method reaches 74 %, which improves the economic performance of production. The total costs for the construction of the plant are about $129 million, and the cost of acetylene is 28,000 rubles/t, which is 29 % lower than the cost of production of acetylene from ethylene. In the process of conversion together with acetylene, a number of products are obtained that can be used for the production of other chemical compounds, and the solid residue can be used as a filler in the production of tires, while the given production costs for acetylene are reduced to 12,200 rubles. With plasma chemical pyrolysis, the largest costs are for electricity - 49 % of the cost. The environmental threat of production is that a strong magnetic field is created to implement the process, the resulting products require purification, while the cost of cleaning acetylene is 16.1 % of the cost. The process uses hydrogen or a mixture of argon and hydrogen to form plasma. The production of hydrogen is a rather complex task, which can be solved by using coke gas formed during coking and containing 55-60 % hydrogen. For the production of hydrogen cryogenic plants are used, in particular the Air Liquide system for the separation of hydrogen from coke gas with a turbo expander. If the company uses coke gas and non-grade coke for the production of acetylene, then a cryogenic plant will be required to separate the coke gas with the release of methane and hydrogen. 1.5-1.55 m^3 of coke gas and about 0.25 m^3 of nitrogen are consumed to obtain 1 m^3 of a mixture containing 75 % H_2 and 25 % N_2, which allows to implement the process of plasma chemical pyrolysis. The cost of the installation is estimated at $40-50 million [6].

Previously coke gas requires cleaning from foreign impurities, it should be taken into account that the volume of coke gas is 1400 m^3/t of coke. For the treatment of coke gas, wet scrubbers operating on the basis of the Venturi principle or vacuum carbonate method are used, which provides the possibility of reducing current costs when using direct coke gas heat instead of steam, while a number of products are obtained during the purification process, which can be processed and have a certain commercial value [7]. This reduces capital costs by 20-30 %, the cost of a coke gas treatment plant can be 160 million rubles. [8].

The second direction of acetylene production is plasma-chemical pyrolysis of methane, either already contained in coke gas or coming from an enterprise producing it from coal seams. In this case, the coke gas passes through the cryogenic air separation unit. Methane from coke gas condenses at temperature -150 °C, goes into liquid state, methane fraction contains 70-80 % CH_4, then it is supplied to the pyrolysis plant [9]. To carry out the process, hydrogen plasma is supplied to the working chamber, while 1 t C_2H_2 requires 1750-2250 nm^3 of hydrogen, the degree of conversion of the raw material to acetylene using this technology is 42-43 %. The creation of a single cryogenic plant, providing two branches of the process, allowing the use of both non-grade coke and coke gas, will significantly reduce the cost of production. The cost of the installation will be $60-80 million.

It is possible to produce acetylene based on the process of gas-phase chemical reactions, comprising generating a supersonic methane stream, providing the supersonic reaction gas stream with energy, sufficient for its activation, the production of acetylene and its release, in which the energy supply of the supersonic methane flow is carried out in this way, that it is accelerated at the same time, its volume is expanded in the course of its movement, and acetylene is obtained by inhibiting supersonic flow of reaction gas. The maximum concentration of acetylene is realized at a distance of 0.68 m from the densification jump and is approximately 31 % of the weight of the feedstock (methane) [10]. The plasma-forming gas is hydrogen. This technology is innovative and promising (the mass fraction of acetylene at a temperature of 1000 °C is 15 %), but technically at the moment it has not been developed and requires further development.

Schemes for plasma-chemical pyrolysis of coal and methane, cryogenic plants for separation of coke gas have been structurally worked out, and their production can be carried out by Russian enterprises such as «Kriogenmash» PJSC, «Ural Chemical Engineering Plant» PJSC, «Penzkhimmash» PJSC, «Kurgankhimmash» LLC, «Kemerovokhimmash» PJSC and several others. This equipment for the production of acetylene using pyrolysis can be produced at Russian enterprises.

In the operation of this equipment, it is necessary to take into account the environmental aspects related to the fact that it operates at high pressures, low temperatures, which can lead to thermal deformation of structures, an increase in the brittleness of the metal at low temperature and destruction of the equipment due to explosion; cryogenic leaks due to equipment depressurization and increased fire hazard. In accordance with these factors, cryogenic equipment must be registered with the Gosnadzor authorities and undergo a technical examination at start-up, as well as periodically [11].

The acetylene obtained in the pyrolysis process is used to obtain the monomer vinyl chloride in the reaction process (formula 1):

$$CH{\equiv}CH + HCl \rightarrow CH_2{=}CHCl + 195\ kJ. \quad (1)$$

This process is carried out in gas and liquid phases in contact apparatus of tubular type. The gas phase method is the most common. The process is carried out in a contact apparatus of a tubular type at 120-220 °C under an excess pressure of 49 kPa over activated carbon impregnated with mercury chloride in an amount of 10 % of the weight of coal [12]. For gas-phase hydrochlorination, dry 97 - 99 % acetylene and highly concentrated hydrogen chloride are used in molar ratio 1:1.1. The reaction products are a gaseous mixture which contains 93 % vinyl chloride and other impurities. The resulting mixture is separated and purified. Vinyl chloride for the production of polyvinyl chloride should contain at least 99.9 % of the monomer and a minimum amount of impurities.

The raw material for the PVC production is hydrogen chloride in addition to acetylene. It is proposed to obtain hydrogen chloride by direct combustion of hydrogen obtained in a cryogenic plant in chlorine supplied through a pipeline with «Khimprom» PJSC, which leads to the production of only hydrogen chloride. In this process anhydrous hydrogen chloride gas is obtained [13]. This process involves a rather complex hardware, since the initial stage of burning chlorine in hydrogen takes place in quartz furnaces, vapor cooling is carried out in ceramic coils, then the cooled mixture is cooled to 180-250 °C supplied to the refrigerator, and then in the heat exchanger entering the cryogenic plant, cooled with nitrogen and condensed at a temperature of -85 °C. Hydrogen chloride is supplied to tanks for storage in liquid form at temperature -850 °C. The cost of the hydrogen chloride plant is $20-30 million according to similar projects [14].

For the production of vinyl chloride from acetylene and hydrogen chloride, synthesis is used, which is a gas-phase heterogeneous catalytic process. The catalyst is impregnated active carbon with an aqueous solution of sulema, followed by drying. The resulting catalyst contained 10 % HgCI2. Due to the high toxicity of sulema and the explosive nature of acetylene, there are stringent requirements for environmental, safety and health requirements. The optimal process is carried out at a temperature of 160-180 °C. The process is exothermic, cooling agents must be used to cool the working substances [15]. Production consists of three main stages: hydrochlorination, hydrogen chloride washing and rectification. The main element of the plant is a reactor, which is a steel shell-and-tube heat exchanger. The catalyst is located in tube space, trans-forming oil circulates along tube space, which is supplied from circulation vessels by means of a central return pump to reactor-heat exchanger circulation system and returned to circulation vessel. The lower part of the reactor is lined with acid-resistant tiles on the lead sublayer in order to avoid corrosion of the apparatus from hydrochloric acid, which is released during the launch of the apparatus and is filled with three layers of ceramic rings. Above the fill rings is activated carbon without catalyst. Upper and lower ends of tubes are filled with the same coal to avoid reaction in uncooled sections of tubes [16]. The cost of a vinyl chloride plant with a capacity of 40,000 t/year is estimated at about 8-12 million rubles or $195,000. The obtained vinyl chloride can be stored for a long time in steel tanks at temperatures of -30 ÷ -50 °C under nitrogen in the absence of inhibitors. Such storage conditions will require capital costs to create a refrigeration plant that stores both liquid hydrogen chloride and the resulting vinyl chloride. The cost of the installation is about 22 million rubles or $300,000.

The final stage of the PVC production process is the vinyl chloride polymerization process, which is carried out in a liquid monomer (vinyl chloride) medium using an initiator, which is diethylhexylpercarbonate, acetanylcyclohexylsulfonyl peroxide, dinitrilazobisobisobutyric acid (porophosphate) The polymerization reaction is exothermic, which requires heat removal, and is carried out at a temperature of 30 ÷ 70 °C. The technological process includes the following stages: preliminary polymerization of vinyl chloride, final polymerization, separation of polymer powder, washing, drying, sieving and packaging [17]. The most common technology is the suspension method. According to the suspension polymerization technology of «European Vinyls» (UK), the polymerization of vinyl chloride dispersed in water is carried out on a periodic basis. The process proceeds at a pressure of 0.5 - 1.4 Mpa, the duration of the process is 20 - 30 hours, and the conversion of the monomer reaches 80 - 90 %. The process scheme uses horizontal or vertical polymerizers with a capacity of 20 ÷ 50 m^3, equipped with a heating jacket and a three-blade scraper stirrer or a tape-spiral stirrer for mixing the reaction mass. Plant consists of polymerization reactor, degasser, hoppers for latex, dryer and cyclone [18]. The cost of the polymerization plant taking into account the fact that the cost of the main equipment - the reactor is 15-20 % of the cost, will be about $600,000 [19].

The monomer and vinyl chloride polymer are quite harmful, carcinogenic substances, they enter the atmosphere as a result of discharge from pipes or reactors in the interval between loads, and are also released from waste water and PVC. This requires in the implementation of the production process the use of degassing methods: the use of a stream of water supplied under high pressure to clean reactors, the development of effective additives that prevent crust formation, to reduce the number of reactor purges, automation of the process and the use of computers; creation of large reactors; use of respiratory devices and remote control of reactors, which will reduce the environmental load on the environment during production [20].

3 Results and Discussion

Analyzing the stages of the PVC production based on carboxylic technologies, it is possible to preliminary calculate the investment costs for this project. But at the same time on the basis of data on raw materials of «KOKS» PJSC (Kemerovo), it is necessary to calculate the material balance in order to determine the predicted volume of PVC production at this enterprise, taking into account the formation of a cluster for the production of this product. Based on the study conducted by the authors, it can be concluded that about 50 million m^3/year of coke gas is burned in a flare, while the gas of this enterprise consists of hydrogen - 57 %, methane - 24 % and other impurities [21]. In this case the volumes of methane and hydrogen that can be used in the PVC production are 12 and 28.5 million nm^3/year respectively. According to the enterprise, coke fines were produced in 2014 about 157 thousand tons, while about 25 thousand tons of coke fines can be used to produce acetylene. To produce 1 ton of acetylene from coal with a carbon content of 60-70 %, 5,000 kg of coal is required, coke will require 3500 kg, and hydrogen - 2000 nm^3, so 7,100 tons of acetylene can be obtained from coke fines, for the production of which 14.2 million nm^3 of hydrogen is required. When producing acetylene by pyrolysis of hydrocarbons in a hydrogen plasma jet, according to «Knapsack-Griesheim» (Germany), methane consumption will be per 1 t of acetylene - 2 t, and hydrogen - 1950 nm^3. In this case the mass of methane extracted from coke gas can be 8.5 million tons, but taking into account the need for hydrogen, given that the integrated use of resources (coke and methane) is proposed, it is possible to produce about 7,000 tons of acetylene. The total production of acetylene will be 14,000 tons. If you use only the technology of plasma chemical production of acetylene from methane, then the yield of the product practically remains the same.

Given that hydrogen is necessary in the production of vinyl chloride, the production of acetylene can be limited to 10,000 t/year. Then 9 million nm^3 of hydrogen remains for the production of hydrogen chloride. Taking into account the material balance, 400 nm^3 of hydrogen is spent on 1 t of hydrogen chloride, then the volume of production of hydrogen chloride can be 22,500 tons. Analysis of the process of production of vinyl chloride, taking into account the costs per 1 t of product 0.45 t of acetylene and 0.67 t of hydrogen chloride, showed that 22,000 t/year of vinyl chloride can be produced from available raw resources [22]. In the production of polyvinyl chloride per ton of product, 0, 479 ton of vinyl chloride is required [23]. In this case, based on the expected vinyl chloride production in «KOKS» PJSC, 45,900 tonnes of polyvinyl chloride can be obtained.

The analysis of the capital cost of equipment for the various stages of the PVC production is shown in the Table 1.

Table 1. Capital costs of the PVC production.

Technological process	**Equipment cost, thousands of dollars**	**Unit costs per ton of PVC, thousands of dollars**	**Adjusted value for planned PVC production, thousands of dollars**
Equipment for coke preparation for pyrolysis	150	0.0033	150
Plasma chemical pyrolysis plant for production of acetylene from coke	129000	0.95	43605
Plasma chemical pyrolysis plant for production of acetylene from methane	95000	0.75	34500
Cryogenic plant for separation of coke gas	75000	1.634	75000
Coke gas treatment plant	260	0.006	275
Hydrogen chloride plant	25000	0.545	25016
Vinyl chloride plant	195	0.0042	193
Refrigeration plant providing storage of hydrogen chloride and vinyl chloride	300	0.0065	298,35
Vinyl chloride polymerization plant	600	0.0131	601,3
Total: coke pyrolysis / methane pyrolysis			145138.65/135933.65

According to the present data, the cost of PVC production, based on the use of plasma chemical pyrolysis of coke or methane, is a capital-intensive project requiring the involvement of a large investor. Nevertheless, a number of chemical enterprises are implementing these projects. An example is «Novaiazot» OJSC (Uzbekistan), which plans to launch the PVC production in 2020. The cost of the project for the PVC production, caustic soda and methanol is more than $500 million. Construction works are carried out by a consortium of Chinese companies China CAMC Engineering Co. LTD и HQC (Shanghai). Commissioning of the enterprise will allow producing 100 thousand tons of polyvinyl chloride (PVC-C), 75 thousand tons of caustic soda, 300 thousand tons of methanol per year. The company will create more than 900 workspaces [24, 25].

4 Conclusions

The PVC production is a very promising and dynamically growing segment of the chemical industry. The innovative aspects of the technical equipment of the PVC production proposed by the authors will reduce the environmental burden on the environment due to the use of monomer and polymer production technologies and assessment of the economic costs of creating PVC production. There are identified ways to reduce energy intensity and capital intensity of this production process due to the use of innovative technologies, in particular plasma-chemical pyrolysis of coke or methane contained in coke gas. The separation of coke gas for the production of methane and hydrogen requires the use of cryogenic plants that have a high cost, and the storage of hydrogen chloride and vinyl chloride requires the use of refrigeration plants. The PVC production will require the development of cooperative ties between the coke chemical enterprise and chemical enterprises in the Kemerovo region on the basis of clustering of the regional economy. The PVC production is an environmentally harmful production, therefore, when creating it, it is necessary to pay great attention to reducing the burden on the environment of the region through environmental protection measures. In the article on the basis of data on similar enterprises the cost of technological equipment was calculated, unit costs per unit of production were determined and the cost of the project to create PVC production based on the raw materials of «KOKS» PJSC was determined. The use of the proposed technology will reduce the burden on the ecology of the region.

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