Scientific justification and effective production technologies of perspective high-quality road bitumens at the modern enterprises with high extent of oil refining.

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ABSTRACT

Ensuring production of high-quality road bitumens for national and interstate roads is becoming more difficult. .
In practice most of Russian crudes are unsuitable for production of distilled bitumens due to the high content of paraffin and the low content of petroleum pitches. Oil refineries have resources components which can be used for producing high-quality bitumens.
A practical method to improve the quality of bitumens offered by authors is the improvement of raw materials through oxidation by an additive of a number of products of production of oils and other processes of crude oil processing (extracts and refined selective treatment of distillate and residual lubricating base oils).
The paper will describe the decision to use of scientific optimization and techniques of quality management of production of road bitumens. Management is conducted by control and regulation of three factors: structure of raw materials of oxidation, kinetics of process of oxidation, composition of the received compounded bitumen. This decision allows to influence each factor of process adequately.
The principle of control of the reactor of oxidation is based on the maximum use of energy of the entering streams and allows to distribute it evenly on all volume of the device. Simplicity of a design of the reactor provides low capital expenditure for its introduction.
The combination of the temperature and hydrodynamic condition of oxidation makes it possible to manufacture a wide range of bitumens of improved quality.

Keywords: Best Available Technology, Industrial application, Equipment

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Almost all refineries of the Russian Federation are currently engaged in processing mixtures of West-Siberian crude oil. Heavy oil residues from vacuum distillation are sent to the production of bitumen and coke. Due to the peculiarities of the West Siberian oil with a low content of resins and asphaltenes, which provides high physical and mechanical characteristics of the bitumens, the main method of obtaining high-quality road bitumen is oxidation of vacuum residues - tars, accompanied by the formation and accumulation in the liquid phase of the resin and asphaltenes.

The best way to improve the quality of road bitumen in the transition to the new standard – GOST 33-133-2014 is the use for the industrial production of bitumen combined approach, which includes both the optimization of group composition of the raw material oxidation, and improving efficiency and controllability of technology the oxidation process.

As shown in [1], optimum tar to obtain bitumen with higher rates of quality of oil from the main oil pipeline of production in Western Siberia content of paraffin-naphthene hydrocarbons 20,0-22,0 % wt., aromatic hydrocarbons of not less than 34,0 % wt., resins of not less than 35,0 % wt. when the asphaltene content is not more than 8,5 wt %. Deepening the selection of vacuum gas oils - increasing the temperature of the end boiling point of from 480 to 560^{o}C leads to increasing the viscosity at 80^{o}C resulting tars from 34 to 302 C (from 779 to 6960 mm ^{2}/s kinematic viscosity).

The group hydrocarbon composition of the tars is approaching the optimum - reduced the content of paraffin-naphthene hydrocarbons from 27 to 8% by weight. and increases the proportion of aromatic hydrocarbons (medium and heavy aromatics with 5 to 14% wt. and from 30 to 33,5 wt.%, respectively). Also increases the asphaltene content (from 3 to 10% wt.) and resins (from 21% to 29% wt.).

But it should be noted that oxidation of such raw materials it is advisable to conduct to increase the asphaltene content of no more than 17 to 21 wt %. [2]. A higher content of asphaltenes with a deficit of resins leads to a risk of insufficient bitumen with elastic-plastic properties and unstable structure. Effective means of regulating the hydrocarbon composition of the raw material oxidation is the introduction of high-viscosity tar in precise calculated amounts of dark and heavy vacuum gas oils [1].

However, practical experience shows that the involvement of the oxidation raw material with optimized composition does not always guarantee a stable production of high quality road bitumen of the required quality with optimum content of groups of hydrocarbons.

The main reasons for this are the low stability of the regime and macrokinetic features of oxidation process of high-viscosity sludge. When you change the performance of the column and change of level of the liquid phase in the apparatus is disturbed steady hydrodynamic mode.

Deteriorating the dispersion in the primary flow of the gas phase is air, transforming as we move through the reactor in oxidation of oxygen-containing gases. And this is observed both in cross section and the height of the apparatus.

Especially noticeable negative changes in the quality of the bitumen by reducing the level of the liquid phase at low pressures and thus local overstatements of temperature and flow fluctuations. I.e. due to the change of temperature and hydrodynamic regime of the process of oxidation of raw materials of the same composition at different capacities and levels of filling of the reactor are often obtained bitumens vary widely in quality. This is confirmed by the results of experimental runs.

As shown, one of the main ways to prevent these negative phenomena is the optimization of the temperature and hydrodynamic regime of the oxidation process through the use of new equipment design of reactors, which allows to increase the efficiency of the overall process [3,4].

The results of the implementation of this technical solution is shown on example of the production of bitumen JSC "******* refinery".

One of the existing columns was reconstructed by installing equipment jet - injection system raw material supply and air. The implementation of this solution provided a significant increase in the efficiency of the machine and receive the following advantages [3]:

• Hydrodynamic and temperature conditions in the reactor allow to obtain based on the existing raw material viscous road bitumen improved quality.

• It is possible to significantly improve the productivity of the machine while reducing specific consumption of air.

• System design injection flow is simple and reliable in operation. One of the advantages of its use is to eliminate the coking problems of the previously used feeder in the column of the air – tube collectors.

• The new design requires little capital costs.

The disadvantage of the modified reactor is that the development of the surface of contact of phases and intensification of mixing occurs only in the lower and the upper zone of the reactor volume. The lack of hydromechanical effects in the Central zone of the reactor leads to coalescence of bubbles of the gas phase and the formation of a jet of upward movement of the gas flow being concentrated in the region of the axis of the housing. The consequence is the appearance of vertical circulation circuits of the liquid in the peripheral zone of the Central part of the apparatus carrying the unreacted mass on column height.

This is especially noticeable when reducing the productivity of the reactor is below a certain limit – the transition to the region of loads of raw materials and air injectors, insufficient for stable operation [5]. To reduce the degree of dispersion and mixing intensity of the phases in the installation of the injectors leads to the deterioration of the Central part of the reactor due to increased jet traffic of the upward gas flow and a vertical circulation flow of the liquid phase. The operation of the reactor as a whole is not stable, in particular, have difficulty maintaining a steady temperature.

To solve this problem in the Central part of the reactor, equipped with injectors of input raw material and air, it was proposed to install specially designed pulsating mixing device is connected to the generator pneumatic pulses, located outside the reactor [6,7].

The disadvantage of this technical solution is the design complexity and the need for the installation of the generator pneumatic pulses, providing the pulse oscillations mixing device.

As a result the objective was to overcome the disadvantages of the embedded reactor [3] with the above described simplification of hardware design [6,7].

This object is achieved in that the reactor equipped with a mounted outside the housing an injector for injecting oxidation gases from the upper part of the reactor circulating flow of bitumen withdrawn from the still portion of the reactor and distribution unit located in the Central part of the reactor to feeding the resulting gas-liquid flow [8].

In Fig.1 schematically shows the proposed reactor, in Fig. 2,3 shows the input units of the raw material and air through the respective injectors, and the main flows of gas and liquid in the area of their installation.

In Fig. 4 is a diagram of the switchgear located in the Central part of the reactor for feeding the gas-liquid stream formed during the injection of gases of oxidation from the top of the reactor by circulating a stream of bitumen withdrawn from the still of the machine. Schematically shows the flow distribution at the outlet of the switchgear.

In the upper part of the cylindrical housing 1 of the reactor (Fig. 1,2) mounted coaxially to the injector input of raw materials, consisting of receiving chamber 2, mixing chamber 3, the diffuser 4 and the nozzle 5 connected to the external line of the feed pipe 6. To the receiving chamber 2 is connected to the pipe 7 with the holes facing the space above the substrate level in the reactor. The diffuser 4, which is attached to the baffle 8, immersed in a gas-liquid medium that fills the reactor.

The injector input of air (Fig. 1, 3) is at the bottom of the reactor and also mounted coaxially with the housing 1. The injector consists of a suction chamber 9, the mixing chamber 10, the diffuser 11 and the nozzle 12 connected to the external line of the air supply pipe 13. The diffuser 11 is attached to the baffle 14.:

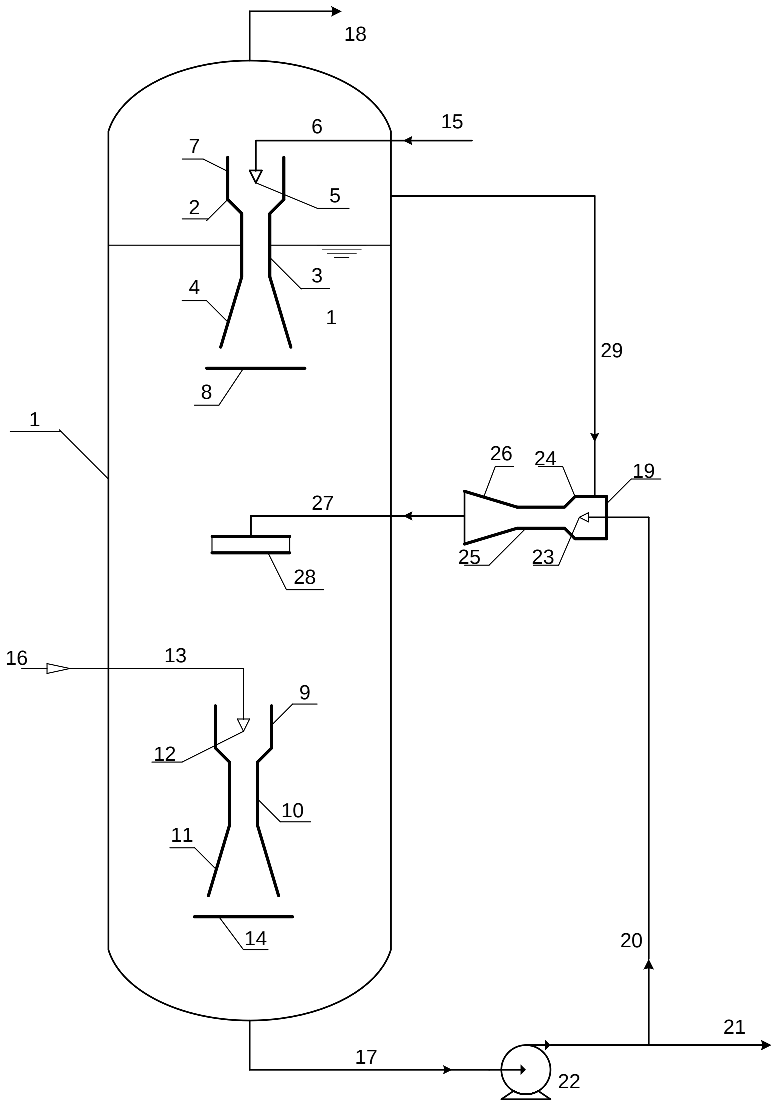

Fig. 1. The scheme of the reactor design (refer to text).

Raw 15 & 16 and the air are supplied through fittings located in the cylindrical part of the reactor.

Oxidized bitumen 17 and oxidation gases 18 are discharged through the nozzles in the lower and upper plate, respectively.

Outside of the reactor vessel installed the injector 19 (Fig. 1,4), connected to a line 20 line 21 pumping pump 22 bitumen still part of the reactor.

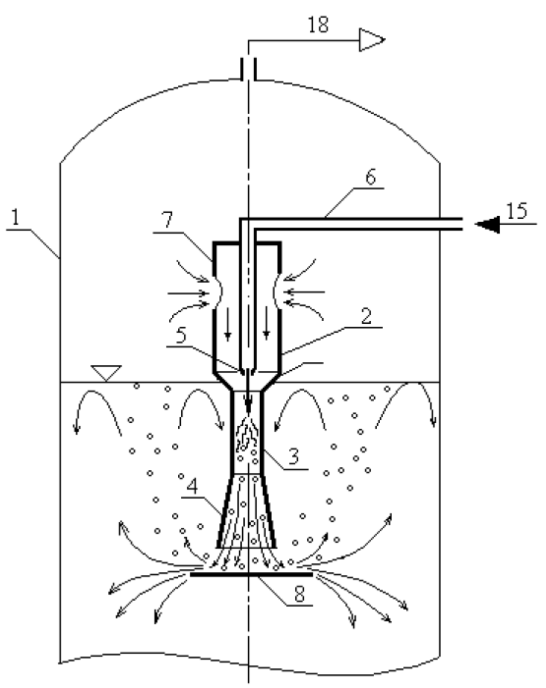

Fig.2. Node input of raw materials through the injector and the main flows of gas and liquid in the area of installation of the injector (designations in text).

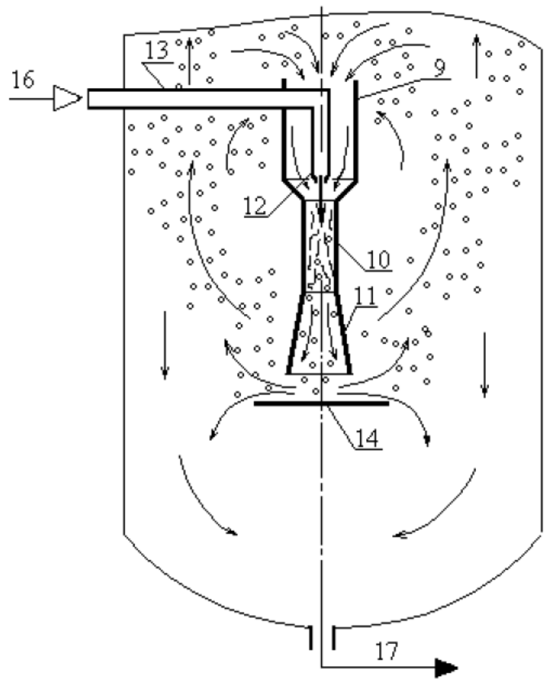

Fig.3. The input node of the air through the injector and the main flows of gas and liquid in the area of installation of the injector (designations in text).

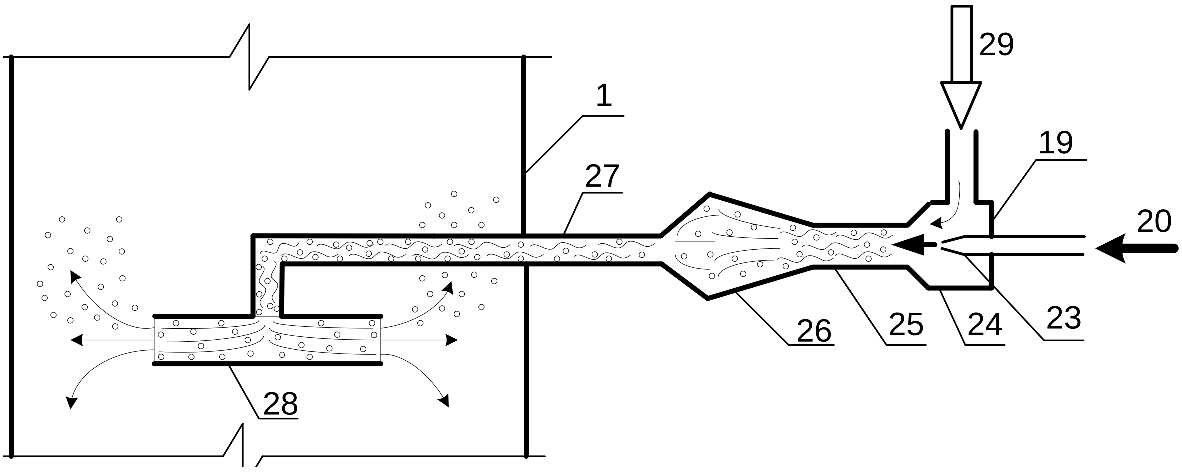

Fig.4.Scheme switch gearin the central part reactor for feeding the gas-liquid flow (refer to the text).

The conduit 20 terminates with a nozzle 23 injects the feed (working) flow of bitumen at the injector 19, consisting of a receiving chamber 24, the mixing chamber 25 and the diffuser 26.

The diffuser 26 is connected by tubing 27 with control device 28. The receiving chamber 24 of the injector 19 conduit 29 connected to the upper liquid unfilled part of the housing 1of the reactor.

The principle of operation of the reactor, the backbone of which is the use of the energy of the incoming flow of raw materials, air and a circulating flow of bitumen, by applying the inkjet apparatus (injectors), is as follows.

A continuously fed reactor materials 15 and 16 air (Fig. 2,3) fall through the respective injectors in the upper and lower parts of the housing 1. Between zones installation of injectors raw material and dispersed in the air make a counter flow movement. Formed during the reaction gases from the oxidation 18 after reaching the level of the substrate leaving the reaction space and discharged from the apparatus. The 17 bitumen obtained in the oxidation process of the raw material by atmospheric oxygen, is pumped by pump 22 from the bottom of the reactor.

Raw 15 (Fig. 2) coming with high speed through the nozzle 5 into the narrowing portion of the receiving chamber of the injector 2 input of raw materials, creates in the cavity of the vacuum chamber. As a result, the pipe 7 connecting the injector with a portion of the reactor filled with raw materials, injections oxidation of gases, containing unreacted oxygen. Formed in the injector raw material gas-liquid mixture in the form of high-speed flow from the diffuser 4 is supplied to the reflector 8. The injection part of the oxidation gases stream entering the reactor raw material leads to the fact that this gas stream containing unreacted oxygen, re-enters the reaction space of the apparatus, increasing the efficiency of used air, as evidenced by a decrease in the concentration of oxygen in gases oxidation 18.

In addition, enhanced mixing in the upper part of the reactor. The volume of the injected gases oxidation considerably exceeds the volume of incoming raw materials and the resulting total gas-liquid flow exiting the diffuser 4 at high speed, the reflector 8 is directed to the periphery of the cross section of the reactor vessel, mixing with the rising gas-air flow from the bottom of the unit.

The share of raw materials entrained by the upward flow of the injected gases to the oxidation, forms a circulating flow in the upper zone of the reactor. In combination with the intensification of mixing it facilitates more complete and uniform oxidation of the feed stream to this zone. The air 16 (Fig. 3) coming with high speed through the nozzle 12 into the narrowing portion of the receiving chamber 9 of the injector air supply, creates in the cavity of the vacuum chamber. As a result, the portion of the feed stream with the gas-air mixture in this zone, injections in the receiving chamber 9.

The resulting gas-liquid mixture through the mixer 10 and the diffuser 11 in the form of high-speed flow is supplied to the reflector 14, distributing it over the cross section of the reactor. A high degree of dispersion of air mixing jets reflected flux and upward gas-air flow, repeated circulation of the air that is entrained into the ejector in the composition of the gas-liquid mixture, provide the intensification and uniformity of oxidation in the zone supply air to the reactor.

The use of incoming energy flows into the reactor through the use of inkjet equipment - injectors - allows to increase the degree of dispersion of the phases in the reaction volume, to intensify the mixing process in the areas of feedstock and air, as well as to create a circulating flow in these zones, providing repeated contact of the reacting phases. Thus in the main volume of the evaporator is maintained countercurrent to the flow of slurry and air.

The circulating flow through the pipeline 20 bitumen (Fig. 1,4) coming with high speed through the nozzle 23 into the narrowing portion of the receiving chamber 24 of the injector 19, which generates in the cavity of the vacuum chamber. As a result, the conduit 29 connecting the injector with a portion of the reactor filled with raw materials, injections oxidation of gases, containing some unreacted oxygen.

Formed in the injector 19 of the gas-liquid mixture from the diffuser 26 in the form of high-speed stream is directed via line 27 to a distributor 28.

The injection part of the oxidation gas stream entering the reactor circulating of bitumen leads to the fact that this gas stream containing unreacted oxygen, again into the reaction space of the apparatus, enhancing the efficiency of the applied air, as evidenced by a decrease in the concentration of oxygen in gases oxidation 18.

In addition, enhanced mixing in the central part of the reactor. The volume of the injected gases oxidation greatly exceeds the volume of bitumen and the resulting total gas-liquid flow exiting the diffuser 26 received within the dispenser 28 is directed to the periphery of the cross section of the reactor vessel, mixing with the rising gas-air flow from the bottom of the unit (Fig. 4). The mixture downstream of the oxidizable raw material received through an injector with bitumen, after separation of the injected gases oxidation, moving in the lower part of the reactor in the region of the air injector.

Work created by the injector 19 hydro-mechanical impact in the Central zone of the reactor leads to additional dispersion of bubbles of the gas phase in order to prevent upward movement of the jet gas flow. The consequence of this is the elimination of the longitudinal contours of the circulation of the liquid phase in the peripheral area of the Central part of the apparatus, leading to the transfer of unreacted mass on column height. Increases the efficiency of operation of the reactor, expressed in the reduction of specific consumption of air for producing bitumen of the required marks and the reduction of oxygen content inoxidation gas.

It should be noted that the injector flow of bitumen can be designed for any desired range of flow rate of the working stream (bitumen), as determined experimentally the optimum amount of bitumen is provided by circulating the capacity of the pump pumping it. In turn, this pump can be selected depending on the required parameters – performance and develop pressure. The scheme of movement of gas and liquid flows in the reactor obtained by combining simulation results of individual major components of input feed streams, is shown in Fig. 5.

Improvement of hydrodynamic and temperature conditions in the reactor provides the possibility of obtaining bitumen of higher quality with improved performance at high efficiency using oxygen of the air supplied to the oxidation.The device of the reactor in comparison with the use of pulsating mixing device is substantially simplified.

Quality indicators of road bitumen produced in the reactor system with injection of feedstock and air , in comparison with the quality of the bitumen obtained in a traditional reactor, are shown in Table 1 .

Table 1 .

Quality of road bitumen produced in the reactor system with injection of feedstock and air , in comparison with the quality of the bitumen obtained in a traditional reactor

Name of indicators	Requirements of standards RNS 2014		Sample 1 injection	Sample 2 injection	Sample 3 tradition	Sample 4 tradition
	70/100	100/130	70/100	100/130	70/100	100/130
1. Penetration, 0,1 мм, at 25 o C	71-100	101-130	76	111	78	118
2. The ring and ball softening point , o C	no less 48	no less 45	49	46	48	45

3. Ductility, sm at 25 o C	no less 62	no less 70	>150	>150	78	100
4.Temperature of fragility, o C	no more -18	no more - 20	-23	-26	-19	-20
5. Flash point. tempe-rature, o C	no less 230	no less 230	279	263	244	241
Temperature resistance to ageing: indicators (at 163 0C, during 5 hours)						
6. Loss of mass sample after warming-up,%, no more	no more 0,6	no more 0,7	0,1	0,2	0,5	0,7
7. Changing the softening temperature after aging, about, o C	no more 6	no more 6	4	5	5	7
8. Temperature fragility after aging, oC	no more -15	no more -17	-22	-25	-16	-19
9. Residual penetration, %	no less 65*	no less 65*	78	73	69	67

As can be seen, the bitumen obtained on newly developed technology , exceed similar bitumens manufactured by the same company according to the traditional technology in terms of elasticity and the brittleness temperature. Especially noticeable advantage in terms of quality, determined after warming up. It should be noted also that the rate of penetration after heating exceeds 73 - 78 % of the initial value.

Conclusions.

1. It is shown that the regulation of the physicochemical properties of the oxidized bitumen is achieved by changing the hydrocarbon composition of the raw material oxidation of heavier tars and the introduction of a fixed amount of distillate components to optimize the ratio of groups of the hydrocarbons in the feedstock.

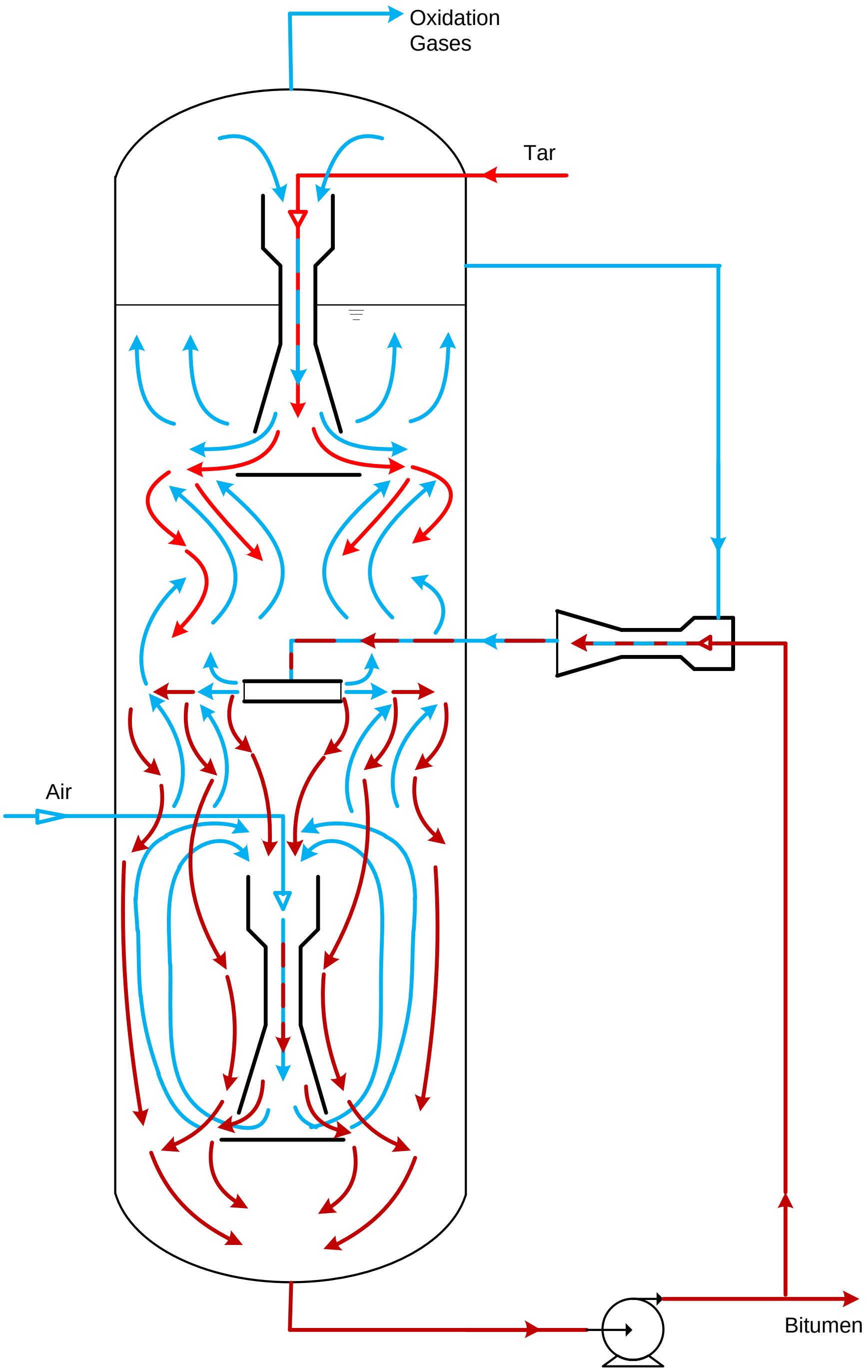

Fig.5. The scheme of movement of gas and liquid flows in the reactor.

2. Improving hydrodynamic regime of the oxidation feedstock is achieved by applying the injection system feed, air and circulating of bitumen, which will, coupled with optimization of the composition of the raw material oxidation, improve the stability of the current quality of road bitumen and bring it to compliance with regulatory requirements of newly introduced GOST 33-133-2014.

3. These data can be used to obtain road bitumen according to GOST 33-133-2014, as well as to develop their production technologies and modernization of industrial production of bitumen oil refineries.

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