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# RELEVANCE AND PROSPECTS OF VISBREAKING PROCESS

Vildanov M.R., Karpov P.V., Poroshin E.A.,Valjavin G.G., Ishkildin A.F.
*Ufa State Petroleum Technological University*

*There is written about most perspective method of visbreaking process increasing yield of light fractions. It is described visbreaking process for residual asphalt production, analyzed properties of produced bitumen. It was made marketing research of domestic and foreign markets of fuel oil.*

Keywords: *visbreaking process, fuel oil, residual asphalt, market of bitumen, tar, mineral additive, ozonization, chemical initiation, physical influence*

At present in front of oil refining complex of Russia the question is stood about considerable curtailment of fuel oil production or its full exception especially sharply. It can be reached by several ways:

- by input of hydrocracker installations new capacities of catalytic cracker which differ by the big capital investments;
- by commissioning of installations of the delayer coking, allowing to increase depth of oil refining to 95 %, and also other updating deep thermal cracker;
- by improvement of visbreaking installations, including reconstruction with release as a residual product of bitumen or a pitch.

The primary aim of thermal processes and visbreaking is increasing quantity of light oil, thereby raising depth of oil refining and profitability of an oil refining complex.

In connection with a wide spread visbreaking process in domestic oil refining, recently a number of authors is offered by rather original and at the same time economic ways of modernization of the given type of process or building new installations similar on capital investments of visbreaking process, increasing depth of oil refining to 86-92 %.

The Russian Federation has experienced strong economic growth rates in recent years despite a global recession. It should enjoy continued strong growth over the next decade. The current strong economic results are due to favorable domestic and international developments. Notable in this regard is the impact of high World oil prices on the Russian economy.

Since the late 1990s primary energy supply has grown by some 2 % per year to reach an estimated 653 MTOE in 2005. Petroleum accounted for about 21 % of primary energy supply and final consumption. The share of petroleum in primary energy has fallen over the last decade, reflecting the trend of displacement by natural gas. The share of final energy consumption has remained relatively stable. District heat is the largest single source of final consumption.

Petroleum is forecast to hold its current share of total primary energy supply in Russia, growing only about 1 % over the period to 2020. Increasing total primary energy supply requires push the consumption of petroleum to around 190 MTOE, compared to an estimated 140 MTOE in 2005 [30].

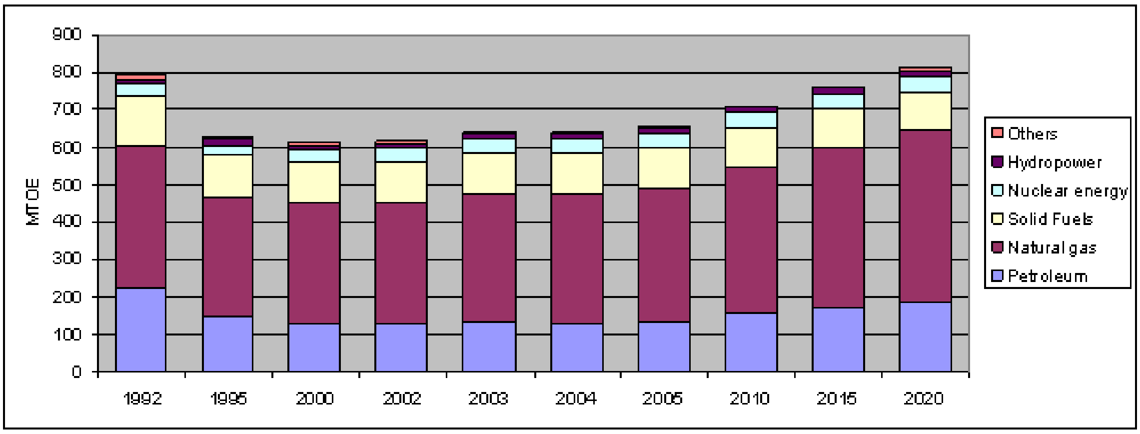


Figure 1. Russia total primary energy supply

Total Russian demand declined from 195 million tons in 1992 to 105 million tons in 1998. This significant decline was due to restructuring of demand, and severe economic recession. Demand has remained close to this level since then, despite a robust economic recovery. While overall demand growth is relatively flat, demand for light products (gasoline, jet fuel gasoil/diesel) has been rising slowly; heavy fuel oil demand has continued to decline. Much of the former oil use in heavy industry and power generation is lost forever by the restructuring in those sectors and plant closures. Some of the oil use remaining will be cut sharply by energy efficiency gains.

Table 1

Structure of the demand of fuel oil in Volga Region

| | 2001 | 2002 | 2003 |
|---|---|---|---|
| Was consumed by industry | 75 % | 72 % | 68 % |
| Including: | | | |
| Power industry | 35 % | 33 % | 33 % |
| Fuel industry | 10 % | 12 % | 12 % |

Analysis of the structure in consumption of oil fuels (motor gasoline, diesel, jet fuel, fuel oil) shows that Volga Region from total consumption consumed.

Table 2

Structure of the consumption of oil fuels in Volga Region

| Name | 2001 | 2002 | 2003 |
|---|---|---|---|
| | % | % | % |
| Motor gasoline | 26 | 30 | 30 |
| Diesel | 35 | 32 | 29 |
| Jet fuel | 2 | 2 | 3 |
| Fuel oil | 37 | 36 | 38 |

Russia has particularly high seasonal fluctuations in oil consumption. In the spring and the summer, there is a higher demand for gasoline and diesel fuels due to the beginning of the agricultural cycle; in the winter the product most in demand becomes fuel oil. These seasonal trends put additional pressure on demand and thus on refinery supply of middle distillates in particular.

In section of Volga Region it is possible to analyze main suppliers of petrochemical products.

Oil Company «YUKOS» supplied for regional markets about 27 % of motor gasoline, 20 % of diesel and 18 % of fuel oil of its total volume supplied to domestic market by this company.

For Oil Company «Bashneftehim» and JSC «Salavatnefteorgsintez» Volga Region is the most preferable market these petrochemical products. JSC «Salavatnefteorgsintez» sold more than 40 % of motor gasoline, about 35 % of diesel and more than 50 % of fuel oil of total sells in domestic market in Russia in 2003.

For the Saratov refinery Volga Region in general was the core market for petro-chemical products: more than 70 % of it volume were sold in region markets.

Comparison of production and consumption oil fuels in Volga Region shows its self-sufficiency. It in the main distinguishes this region from others regions of Russia.

Table 3

Structure of supply of fuel oil by JSC «Salavatnefteorgsintez»

| | 2002 | | 2003 | |
|---|---|---|---|---|
| | Thousands ton | % | Thousands ton | % |
| **Total** | **1 750** | **100** | **1 490** | **100** |
| **Russian federation** | **1 590** | **90** | **1 410** | **95** |
| Northwest Region | 255 | 15 | 340 | 23 |
| Volga Region | 995 | 57 | 730 | 50 |
| *Bashkortostan* | *675* | *39* | *500* | *33* |
| **Export** | **160** | **9** | **80** | **5** |
| *Outside CIS* | *78* | *4* | *45* | *3* |

Supplies of fuel oil for export are small in as compared with consumption its on Russian market.

The main products of Russian export are diesel and fuel oil, and the main market for Russian oil products is Western Europe. Meanwhile Russia supply about 60 % of import diesel oil and a half of fuel oil to this region [33].

In perspective until 2020 there is no any premise for preservation high growth rate of export of oil products. Main export will be from refineries placed near of seaside terminals and with use oil pipelines, as well as by river in season. Export oil products from refineries placed deep inside in Russia and refineries which have no effective transport scheme will have tendency to decline.

Refinery industry in Russia fully satisfies oil products demand of the country. Excess of its production over real consumption is more than 150 %. Import is minor (about 0.5 million tons) and it is less than 0.3 % of total consumption of oil products, and generally in Far East.

Annual heavy fuel oil use in Russia has collapsed from over 70 million tons in 1992 to an estimated 18 million tons today. Most of the decline can be attributed to restructuring of the economy away from the heavy military-industrial complex, and by substitution of oil by natural gas in the heat and power sectors. Over this period, reduced economic activity also contributed to the reduction in demand [30].

As fuel oil use in heat and power has been partially displaced by natural gas in recent years, the shares of fuel oil use by region have changed. In the late 1990s the Central and Volga regions (the major power-producing regions) accounted for over 40 % of fuel oil consumption. Today these regions have declined to about 37 %. The Northwest now accounts for the major share.

Table 4

Regional distribution of consumption fuel oil in Russia

| Region\year | 2000 | 2001 | 2002 | 2003 | 2004 | 2005 | 2010 | 2020 |
|---|---|---|---|---|---|---|---|---|
| Central | 3,9 | 3,2 | 2,7 | 2,6 | 2,5 | 2,4 | 3,3 | 3,4 |
| Northwest | 6,5 | 6,3 | 6,9 | 6,2 | 5,0 | 4,8 | 6,4 | 6,3 |
| South | 2,2 | 1,7 | 1,2 | 1,1 | 1,1 | 1,1 | 1,5 | 1,7 |
| Volga | 6,3 | 5,9 | 5,5 | 5,0 | 4,4 | 4,2 | 56 | 5,7 |
| Urals | 1,1 | 1,2 | 0,9 | 0,9 | 0,8 | 0,7 | 1,0 | 1,2 |
| Siberian and Far East | 6,6 | 6,5 | 5,3 | 5,5 | 4,9 | 4,6 | 6,3 | 6,4 |
| **Total** | **26,7** | **24,9** | **22,6** | **21,2** | **18,8** | **17,8** | **24,1** | **24,8** |

The expected increase in gas prices from their current very low levels is expected 1o result in some moderate recovery of fuel oil demand in the heat and power sector.

Table 5

Dynamics of domestic price for natural gas in Russia,
US dollars per 1000 cubic meter

| | 2006 | 2010 | 2015 |
|---|---|---|---|
| Average European price | 292 | 225 | 203 |
| Transport costs | 25 | 33 | 33 |
| Export duty | 73 | 56 | 51 |
| Export netback | 194 | 136 | 120 |
| **Russian domestic price** | **43** | **79** | **120** |
| Domestic discount | 78 % | 58 % | 100 % |

In forecast of socio-economic development of Russian Federation for 2008, parameters of forecast until 2010 and ultimate price levels for production of natural monopoly subjects» were provided for next parameters of changing prices:

– 15 % after 1 January 2007; – 25 % after 1 January 2008;

– 13 % after 1 January 2009; – 13 % after 1 July 2009;

– 13 % after 1 January 2010; – 13 % after 1 July 2010.

It is planned increase gas sale profitability on Russian market up to European level by 2011 (with a glance of transport cost and export netback) [31].

This price increase had already given increase in consumption of fuel oil in energy industry.

Russian fuel oil is generally of high sulfur content. In a similar manner to diesel above, fuel oil netback export prices have been forecast on the appropriate European high sulfur fuel price.

Salavat data indicates that domestic fuel oil sales have been at a discount to the export parity price. With the forecast increase in domestic gas prices (see below). We envisage that firmer fuel oil prices can be achieved in the future. Domestic fuel oil prices are expected to increase relative to export parity sales, but remain discounted in the longer term to the energy parity price of gas by around 30 %.

The consumption of heavy fuel oil in Europe has declined considerably over recent years in all sectors except for bunker fuel. In the forecast period the decline in inland consumption is expected to continue at a slower rate as much of the substitution has already occurred. The following table summarizes historical and forecast fuel oil demand.

Table 6

Fuel oil consumption in Europe, million tons

| | 1995 | 2000 | 2005 | 2010 | 2015 | 2020 |
|---|---|---|---|---|---|---|
| Power industry | 54,6 | 38,6 | 27,4 | 22,0 | 19,2 | 17,4 |
| Heavy industry | 34,6 | 29,1 | 26,4 | 23,6 | 21,5 | 19,8 |
| Transport | 1,5 | 1,0 | 1,3 | 1,3 | 1,3 | 1,3 |
| Marine | 28,2 | 35,6 | 45,4 | 51,4 | 53,2 | 55,7 |
| Others | 9,4 | 5,5 | 5,5 | 6,0 | 5,6 | 5,3 |
| **Total** | **128,3** | **109,8** | **106,9** | **104,2** | **100,7** | **99,4** |

Overall fuel oil use declined by over 20 million tons to 107 million tons, between 1995 and 2005, with large falls in electricity generation and the industrial sectors. Over the same period, bunker fuel use increased by 17 million tons (equivalent to 5 % per year) to reach 45 million tons.

In the forecast a decline in use across Europe is expected to continue in all sectors except for bunkers. However, the rate of decline is expected to ease because in the past restructuring in Eastern Europe contributed to very rapid declines. As the economies in the East continue to restructure, fuel oil use may increase slightly as electricity demand increases more quickly than new alternative fueled capacity can be built.

Bunker fuel is expected to continue to grow as the European economy expands. Growth over the forecast period is expected to average 1.3 % per year.

Air quality has been an important issue for the European Union member states for some time and this has resulted in a large number of specific directives. Heavy fuel oil has, and will be affected by these directives and the various national laws and regulations that arise from them. The most direct impact is on the level of sulfur in heavy fuel oil and heating gasoil.

The main impact on the quality of heating gasoil and heavy fuel oil has been from the sulfur content of Liquid Fuels Directive. The latest update required all heavy fuel oil sold inland to be no more than 1 % sulfur [32].

The DG Environment of the European Commission has identified emissions from ships as a major contributor to the overall sulfur oxide ($SO_x$) emissions in the EU.

Annex VI ("Regulations for the Prevention of Air Pollution from Ships") of the MARPOL 73/78 Convention mandates the overall maximum sulfur content in marine bunker fuel to 4.5 %. The main impact in relation to residual bunkers is the imposition of a 1.5 % S maximum in the SECA areas [32].

Russia is a significant exporter of gasoline, gasoil/diesel and fuel oil. Much of the exports to the West are destined for the major refined product markets of Europe and the United States. In table below provides a forecast of trade for the main refined products with respect to Russia, Europe and the United States.

Table 7

Oil products trade balance - import/(export), million tons

| | 2002 | 2003 | 2004 | 2005 | 2010 | 2020 |
|---|---|---|---|---|---|---|
| **Russia** | | | | | | |
| Gasoline | (3,3) | (3,9) | (4,1) | (5,5) | (5,3) | (3,8) |
| Jet fuel | 0 | 0 | 0 | 0 | 0 | 0 |
| Diesel | (28,8) | (30,0) | (29,4) | (32,9) | (29,2) | (21,2) |
| Fuel oil | (34,3) | (31,9) | (30,9) | (36,2) | (38,0) | (39,4) |
| | | | | | | |
| **Europe** | | | | | | |
| Gasoline | (22,7) | (26,4) | (33,3) | (37,8) | (44,9) | (44,0) |
| Jet fuel | 10,2 | 10,5 | 11,8 | 14,7 | 18,0 | 24,6 |
| Diesel | 21,9 | 24,8 | 24,7 | 28,4 | 39,8 | 52,8 |
| Fuel oil | 8,1 | 0,8 | (7,5) | (7,0) | 5,8 | 9,3 |
| | | | | | | |
| **USA** | | | | | | |
| Gasoline | 16,0 | 16,8 | 15,9 | 20,0 | 19,1 | 21,5 |
| Off-grade Gasoline | 10,5 | 12,9 | 16,5 | 20,4 | 20,1 | 10,8 |
| Jet fuel | 3,6 | 4,0 | 3,9 | 4,5 | 3,1 | 3,5 |
| Diesel | 7,6 | 11,1 | 10,6 | 9,2 | 11,9 | 16,3 |
| Fuel oil | 3,9 | 7,1 | 12,1 | 15,1 | 9,0 | 7,2 |

It is providing for development refinery industry for supply perspective levels of domestic demand in Russia, and the first of all on the base of increasing of crude oil use efficiency. As a priority it will be successive increase quality of motor fuels according to motor vehicles fleet changes with the preservation of technologically justified use of fuel oil as a reserve fuel in power industry.

The most developed and reliable technologies of visbreaking [17, 28] belong to companies Shell/ABB and FW/UOP.

So in the end of 2008 year in JSC "Salavatnefteorgsintez" installation of visbreaking on technology Shell Global Solution has been constructed. Distinctive feature of the given technology are application of internal devices in the soker-chamber, possibility of regulation of pressure separately in the furnace and in the soker section, and also an effective design of the furnace that allows to increase overhaul period of installation to 9-12 months.

At present there is a set of workings out allowing considerably to improve process of visbreaking. The steadfast attention last years is given, for example, to processes ozonize [25] of the residue. The intensification of target processes by application of physical methods is considered. Recently it is offered to apply the phenomenon of cavitations [2] to these purposes, and also electromagnetic influence on raw materials. Also it is offered to use an ionizing radiation [1, 4], for example bunches accelerated electrons.

For today following additives [3, 13, 14, 16, 27] in raw materials of visbreaking are standard, allowing to increase an exit of light fractions a little and to lower coke formation:

- various oil fractions (the aromatic fraction of catalytic cracker, hydrocarbons of some naphthalene, 3 % water emulsion of black oil, tetralin)
- oxygen-containing additives (organosiloxanes , spirits, ketones, acetone)

An expert of Technological Mountain University (Germany) has carried out basic research of combined processing of the residue and plastics. It is shown that the synergetic effect gives the chance to attain more a deeper cracking of the residue without coke formation. The higher exit of light products is besides attained. The atoms of hydrogen entering into a molecule of polymer increase relationship H/C in raw materials. Reactive products of cracking of plastic [15] stabilize asphaltenes which are responsible for coke formation. The best results are gained at using of plastic mixes. So-called initiation of depolymerization in a mix is a principal cause of observed synergetic effect.

Visbreaking process also spends in the presence of hydrogen [18] that allows to get rid completely practically from coke formation. Hydrogen at 425-450 ºC is energised hardly but one manifests sufficient activity at interacting with the hydrocarbon radicals formed as a result thermodestruction. It leads to substantial growth of an exit of petrol fraction and practically to absence coke products even at 450 ºC. The wide propagation got donor-solvent processes of visbreaking [11] such firms as Lurgi processes (DSV), firms Exxon (HDDV), firms Gulf Canada (DRB). As hydrogen donators act gas oil fractions catalytic and thermal cracking subjected to selective hydrogenation and the aromatic fractions also.

Basic new physical and power methods now are developed for raise of efficiency of process of a visbreaking: ultrasonic, electromagnetic, electron beam, laser, cavitations, etc.

The composition of the residue is much combined and to operate process as much as possible effectively it is necessary to know in details mechanisms of thermal and physical affecting on raw materials.

Controlling temperature and duration of cracking it is possible to change quality of products essentially. So in process of "Visbreking-TERMAKAT" cavitation-acoustic affecting [10,12] on raw materials is applied, thereby energy is brought to molecules not only thermal but also mechanical depositing at a collapse of cavitations bubbles. Generally chemical bond rupture can be carried out only mechanical affecting at intensity of ultrasonic affecting equal to a binding energy. Thus the thermocracking temperature decreases and thermocondensation choke also and thus coke formation practically completely stops, the exit of light fractions attains 85 % wt. per fuel oil and in the capacity of the rest is made residual asphalt. Ultrasonic affect is applied in stabilization of boiler fuel preventing formation of the colloid structures also.

One of the most actual now ways of conversion of the residue is thermocracker of residue with stage of initial initiation by ozone. Efficiency of the given way was repeatedly proved at a stage of laboratory and pilot tests. The residue is saturated ozone in quantities of 0.2 - 15 g/kg of the raw materials, thus a necessary condition is presence sulfur-containing compounds [25, 29] in raw material in number of not less than 0.65 % of weights. Compounds formed in the course of ozonization decompose at lower temperature that gives the chance to carry out thermocracking of the residue in the industry at temperature 420 – 440 $^{o}$C . Thus the exit of light fractions increases to 60 % at thermal processing of atmospheric residue, and makes 40 % and more for vacuum residue. It is necessary to note practically full suppression of reactions of coke formation and decreasing in the maintenance of sulphur in heat treatment products that has great value at conversion high-sulphur oils. Unique obstruction of a wide propagation of the given technology are low efficiency of ozonizer and the big expense for the electric power and only complex use products of ozonator allows to gain essential profit at the factory.

Other approach to regulating of kinetics of the thermal process offered by a number of authors consists in chemical initiation of cracker process of oxygen of air. At contact of oxygen to the residue are formed hydroperoxides which at cracking temperature at once disintegrate on radicals initiating further thermocracking raw materials at lower temperature with higher speeds and retarding consolidation process. Thus the residue is oxidized asphalt and an exit of motor distillates makes more than 40 % that deepens oil refining [9] approximately on 20 %.

In Russia original process of thermochemical processing of the residue in a mix with slates or sapropelite coals is developed in which basis process «TEKSLAN» lays. As a result of numerous experiments it has been established that organic and mineral parts [26] of these hard combustible fossil (slates and sapropelite coals) in the field of temperatures 390 - 440 ºC have activating influence on thermal transformation of heavy residual and a liquid high-boiling wastes of some petrochemical manufactures. The combination of such properties has shown that applying any slates or sapropelite coals containing 12-70 % of an organic part is possible to carry out process with a high exit of target production without intensive coke formation.

As the active additive it is possible to use various slates and sapropelite coals taken in quantities of 4-25 % on the residue. Deposits of these hydrocarbonic raw materials are available on all territory of the Russian Federation.

Similar initiating influence renders natural zeolite which use as the additive to raw materials.  The catalyst is inducted into initial raw materials in quantities of 1-20 %. The way [8] provides a high exit of light petroleum derivatives without intensive coke formation. Also apply the catalyst gained by enrichment molybdenum, cobalt, and nickel or tungsten ores [5, 6, 7], containing (%): 1.2-2.8 iron and 3.8-58.0 silicon. Catalysts as a rule comminute to corpuscles a size 100-1000 microns and mix with raw materials.

With the occurrence of "soft" cracking process was named visbreaking of the heavy residues (tars, etc.) it became reasonable to estimate quality of received bitumen under the scheme «visbreaking - high-vacuum distillation» and possibility of their application. Bitumen which are received under the given scheme concern to not oxidized and in many parameters surpass the oxidized ones. It is necessary to notice, that abroad production of not oxidized bitumen is the main.

At work by a bitumen variant, the bitumen recovery is 70-75 % on initial tar (depending on a kind of oil and the tar submitted to visbreaking). Besides, it is received up to 20 % of heavy gasoil which can be used as a thinner or a crude component for production of motor fuels.

It is necessary to notice also, that production of bitumen with visbreaking of tar with the subsequent atmospheric or vacuum distillation allows to reduce environmental pollution, first of all at the expense of an elimination of emissions of considerable volumes of oxidation gases (80 - 150 $nm^3/g$), taking place in a traditional way of bitumen production with a purge air [19].

As visbreaking bitumen are received by vacuum (or atmospheric in some cases) distillation of visbreaking residues, they by the nature are so-called residual bitumen (unlike the traditional oxidized bitumen), and basically meet the requirements of operating State Standard 22245-90 «Oil road viscous bitumen» for marks BN [21], at the same time have characteristic features, namely [19, 20, 21]:

- Excellent coupling (adhesion) with mineral materials of sour breeds (sand, a granite, etc.), most often applied in road building (the oxidized bitumen especially from asphalt of propane deasphalting, practically have no adhesion to such materials);
- Increased deformability on plastic type (an extensibility at 25 ºC more than 100 sm while the oxidized bitumen have values from 45 to 65-70 sm);
- Preservation of a high extensibility and adhesion (coupling) after ageing in the standard tested conditions. Change of temperature of a softening and penetration at 25 °C after warming up basically keep within typical requirements to road bitumen.

It is necessary to notice, that visbreaking bitumen on colloid stability (stratification on Oliensis's ring) concede oxidized [22]. At the same time operational tests standard asphaltic concrete samples on visbreaking bitumen in climate cell, spent in Russia Road Research Institute, have shown their sufficient stability to action of climatic factor (sign-variable temperatures from -20 to +60 ºC , Uf - and Ik-radiation) higher, than at the comparative sample of the oxidized bitumen of mark BN 60/90 [20].

Process «tar visbreaking - vacuum distillation» for the purpose of production of bitumen has been fulfilled at production TK-2 unit JSC "New Ufa Refinery", have been developed more than 400 tonnes road bitumen on specially developed specifications 38.401-66-88-92 "Oil road bitumen with the improved adhesion and deformability BDA» [20] . The cost price of visbreaking bitumen approximately on 15 % below of cost oxidized bitumen.

On conclusion of Russia Road Research Institute bitumen BDA can be applied at the installation of the top layers of coverings of highways III - IV technical categories in III - IV road-climatic zones, at the installation of the bottom layers of any roads, for surface treatment, for country roads, etc. [20].

Various variants of involving of the visbreaking residues (VR) in bitumen production [23, 24] have been tested at Moscow Refinery:

1. Blending of concentrated VR with the marketable oxidized bitumen (to 50 %), that allows to produce the road standards-driven bitumen, before and after warming up;

2. Direct oxidation relatively light VR which is have boiling point above 360 ºC with standard bitumens production of type BND, but with the increased extensibility;

3. VR oxidation mix with boiling point above 360 °C with tar and bitumen production of type BND;

4. VR reoxidation to temperature of a softening around 70 – 72 ºC and its dilution with tar that allows to produce bitumen of marks BND with a quality stock of an extensibility [24].

At work by a bitumen variant the additional quantity of distillate fractions which can be used in secondary processes or as thinners is developed also.

Thus, visbreaking process for refining of the heavy oil residues, improved for more yield of motor fuels, is the actual direction of oil refining promoting for increase of refining depth.

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