Development of Arctic Diesel Fuel with Optimal Composition

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Abstract. The article offers the possibility of obtaining Arctic diesel fuel, which can be used at low temperatures. The physico-chemical properties of the resulting diesel fuel are also shown. New technical conditions were developed for a new type of Arctic diesel fuel. The main indicators of the quality of low-carbon diesel fuel are low-temperature properties, estimated by cloud point, temperature and temperature limit. New arctic fuel was obtained by adding a depressant. We used the depressor additives Keroflux and Difron. When selecting a depressor additive for a new grade of diesel fuel, it was necessary to take into account not only the composition of the fuel, but also the particular structure and composition of the additives themselves. Studies by many authors have shown that the solubility of additives based on copolymers of ethylene with vinyl acetate is lower than that of copolymers of vinyl acetate with alkyl methacrylate. The article also shows the possibility of obtaining basic fuel with a given pour point directly on the direct distillation of oil. An innovative jet hydraulic mixer was used to mix petroleum products, which provides intensive mixing of petroleum products in tanks and ensures stable quality of petroleum products during storage. Such technology allows to obtain winter and arctic varieties from summer diesel fuel by adding depressor additives.

1. Introduction

The development trend of vehicles in the North is the increasing use of diesel engines, which consume 30-35\% less fuel compared to carburetor engines and have low exhaust gas toxicity [1].

To ensure reliable and economical operation of a diesel engine, diesel fuel must meet the following requirements: have good mixing and flammability; have a suitable viscosity; have good pumpability at various ambient temperatures; contain as little as possible sulfur compounds, water-soluble acids and alkalis, mechanical impurities and water.

Some of the main disadvantages of diesel fuels are some of their properties, which lead to difficulties starting diesel engines in winter time [2]. Therefore, diesel fuels are produced with different characteristics depending on the season. They are almost the only petroleum products that have seasonal requirements for their quality indicators [3].

In Russia, there is a shortage of winter diesel fuels. For winter diesel fuels, special requirements have been developed for low-temperature properties - cloud point, pour point, and limiting filterability temperature.

There are several ways to bring the quality of diesel fuels to the necessary requirements for winter varieties [3]. The most common way is to facilitate the fractional composition. At the same time, diesel fuel resources are reduced by 25\% [3]. During hydrodewaxing, the resources of diesel fuel are reduced to 18\% [4]. The use of carbamide dewaxing and dewaxing on zeolites leads to non-selective
extraction of paraffin hydrocarbons from fuels, including and low molecular weight responsible for the cetane number [5]. In addition, with the help of carbamide dewaxing cannot provide the necessary requirements for cloud point. An alternative to all these methods is the introduction of depressants into the fuel. [6].

There is a lot of research in this area. However, earlier work on the production of diesel fuels with depressant additives is mainly devoted to the manufacture of winter fuel based on summer fuel. A promising direction for obtaining low-temperature diesel fuels is the use of local resources, namely, its production from the oil of the Talakanskoye field of the Sakha Republic (Yakutia).

The work was done in accordance with the “Investment Strategy of the Republic of Sakha (Yakutia) for the period up to 2016 and the main directions until 2030”, adopted by Decree of the President of the Republic of Sakha (Yakutia) No. 2864 dated September 11, 2014, and the “Strategy of Social and Economic Development Of the Far East and the Baikal Region for the period up to 2025 ”approved by the Decree of the Government of the Russian Federation N 2094-p dated December 28, 2009.

2. Materials and methods

The development of new winter and arctic diesel fuels requires the installation of technical requirements for their quality. The main indicators of the quality of low-carbon diesel fuels are the low-temperature properties estimated by the cloud point, the freezing point, and the limiting filtration temperature [7, 17-20].

Taking into account foreign and domestic experience in the use of diesel fuels with depressant additives, 2 indicators were selected when developing a technical condition for Arctic fuel:
- limit filtration temperature
- freezing temperature

**Table 1. Requirements for a new type of low-fouling diesel fuels with depressant additives (prototype).**

| The name of indicators                                      | DAp-53\%-39 |
|-------------------------------------------------------------|-------------|
| Fractional composition:                                     |             |
| 50% distilled at temperature, °C, not higher                | 240         |
| 96% distilled at temperature (end of distillation), °C, not higher | 340         |
| Kinematic viscosity, mm² \ s (cSt)                          | 2,5-3,5     |
| Mass fraction of sulfur in fuel,%, not more than:           | 0,2         |
| Tests on a copper plate                                     | stands      |
| The content of water-soluble acids and alkalis              | The absence of |
| Actual resin concentration, mg per 100 cm² of fuel, not more than | 24…25      |
| Coking ability, 10% residue,%, not more than                 | 0,3         |
| Content of mechanical impurities                            | The absence of |
| Water content                                               | The absence of |
| Flash point, °C not higher                                  | 30          |
| Kg density / m², not more                                   | 816         |
| Pour point, °C not higher                                   | -53         |
| Extreme filterability temperature, °C                       | -39         |
| Acidity, mg KOH per 100 cm³, not more                       | 2,0         |
| Iodine number, g of iodine per 100 g of fuel, not more      | 1,5         |
Technical conditions standardize all the main indicators of diesel fuel quality: cetane number, fractional composition, viscosity, mass fraction of sulfur, content of mechanical impurities and water, acidity.

Table 1 shows the requirements we have developed for Arctic diesel fuel DAp-53 \(-39\) (the pour point is indicated in the numerator, the limiting filtration temperature is indicated in the denominator). Technical specifications were agreed with all interested organizations.

Fuel with a freezing point not higher than minus 35 °C is made by compounding a straight-run fraction of 140-270°C and hydrotreated diesel fuel in the ratio from 88:12 to 83:17 [7].

The creation of a new grade of low-carbon diesel fuel requires the selection of a fuel with a pour point of \(-28\) and selection, taking into account the hydrocarbon composition, the most effective depressant additives.

It is possible to obtain base fuel with a given pour point directly at the distillation units. Table 2 shows the main indicators of the quality of the components of the basic diesel fuel DAp-53 \(-39\).

**Table 2.** Physico-chemical quality indicators of the basic component of diesel fuel DAp-53 \(-39\).

| The name of indicators                                      | Components                        |
|-------------------------------------------------------------|-----------------------------------|
|                                                             | Kerosene distillate 180-220 °C | Light atmospheric gas oil 220-280 °C |
| Kg density / m², not more                                    | 815                               | 817 |
| Kinematic viscosity, mm² \(s\) (cSt)                        | 2,798                             | 2,699 |
| Pour point, °C                                              | -25                               | -27 |
| Extreme filtration temperature, °C                         | -15                               | -18 |
| Flash point, °C                                             | 28                                | 29 |
| Fractional composition °C: start of boiling                 |                                    |     |
| 50 %                                                        | 234                               | 245 |
| 96 %                                                        | 330                               | 347 |
| Group composition of HC C, vol.%                            |                                    |     |
| The amount of saturated HC                                  | 94,21                             |     |
| N-alkanes                                                   | 67,36                             |     |
| Isoalkanes (2-3 methyl)                                     | 8,54                              |     |
| Isoprenoid                                                  | 16,48                             |     |
| Cycloalkanes                                                | 1,83                              |     |
| The amount of aromatic HC                                   |                                    |     |
| Alkyl benzene                                               | 4,46                              |     |
| Alkynaphthalenes                                            | 1,60                              |     |
|                                                            | 2,86                              |     |

As can be seen from the table, straight-run fractions have rather low freezing and filtration temperatures. The ratio of kerosene distillate and kerosene fraction (intervals from 180 °C to 280 °C) was chosen in such a way as to obtain a summer diesel fuel with a low flash point, which implies a high fire safety.

Thus, fractions of light gas oil and kerosene fractions are involved in the creation of the new type of Arctic diesel fuel DA-53 \(-39\).

Two types of product depressor additives were used: Keroflux 6100 and Difron 315. The results of studies of the effect of depressants are shown in Tables 3-4.
Table 3. Low-temperature properties of diesel fraction from Talakan oil with Keroflux 6100 depressant additive.

| Try | Additive concentration | Name of the indicator          | Pour point, °C | Extreme temperature, °C | Filtration |
|-----|------------------------|--------------------------------|----------------|--------------------------|------------|
|     |                        |                                |                |                          |            |
| No additive | -                      |                                | -28           | -17                      |            |
| 1   | 0,10                   |                                | -36           | -20                      |            |
| 2   | 0,20                   |                                | -39           | -25                      |            |
| 3   | 0,50                   |                                | -35           | -24                      |            |

Table 4. Low-temperature properties of diesel fraction from Talakan oil depressant Difron315.

| Try | Additive concentration | Name of the indicator          | Pour point, °C | Extreme temperature, °C | Filtration |
|-----|------------------------|--------------------------------|----------------|--------------------------|------------|
|     |                        |                                |                |                          |            |
| No additive | -                      |                                | -28           | -17                      |            |
| 1   | 0,10                   |                                | -45           | -33                      |            |
| 2   | 0,20                   |                                | -46           | -33                      |            |
| 3   | 0,40                   |                                | -47           | -34                      |            |
| 4   | 0,45                   |                                | -48           | -35                      |            |
| 5   | 0,5                    |                                | -51           | -38                      |            |
| 6   | 0,55                   |                                | -53           | -39                      |            |
| 7   | 0,6                    |                                | -50           | -34                      |            |
| 8   | 0,7                    |                                | -39           | -31                      |            |

When selecting the depressant additive for diesel fuel DAp-53 / -39, it was necessary to take into account not only the composition of the fuel, but also the characteristics of the structure and composition of the additives themselves. Many studies have shown that the solubility of additives based on copolymers of ethylene with vinyl acetate (EVA) is lower than that of copolymers of vinyl acetate with alkyl methacrylate (CBA). Thus, EVA copolymers are good formulators of paraffin embryos for summer diesel fuels with a cloud point of minus 4, and CBA-based additives are suitable for diesel fuels of a lighter fractional composition. As can be seen from the tables, the injectivity of both additives is good, which is related on the one hand to the composition of the additives, as mentioned above, on the other hand to the molecular weight distribution of n-paraffin hydrocarbons.

One of the most important indicators determining the injectivity of depressor additives in diesel fuel is the content of n-alkanes and their molecular mass distribution in diesel fuel. Table 4 shows that there are differences between low-melting, medium-melting and high-melting n-alkanes. It is known that fuel with a broader molecular weight distribution has a better injectivity for depressors. A high-melting n-alkanes determine the course of the crystallization process in the fuel. According to Burov A.A. effectiveness of the additive is related not only to the distribution of n-alkanes, but also to other groups of hydrocarbons constituting the fuel. Fuels with a high content of unbranched aliphatic structures and a higher content of naphthenic hydrocarbons have the best injectivity of additives, and the predominance of isoalkane structures worsen the injectivity of fuels to depressant additives [9].

As can be seen from the tables, it is observed that as the concentration of the additive increases, the pour point and the maximum filtration temperature, reaching a maximum, worsen. So, depressant additive Keroflux 6100 reaching its maximum TK minus 39, and PTF minus 25, at a concentration of 0.2% wt., while with increasing concentration of the additive low-temperature indicators worsen. Difron 315 depressant additive has the same nature of changes in low-temperature properties, however, its maximum is achieved with the introduction of 0.55% of the mass of additives [10]. This can be explained by the fact that in the "n-paraffin hydrocarbons - additive" system, processes characteristic of colloidal systems take place: the excess of the free surface energy of the system is
compensated by the adherence of the additive micelles. The rate of formation of the dispersed phase at these fuel temperatures is maximum, which leads to the creation of a large number of small crystals, the distance between which decreases sharply with increasing concentration of the additive. Additive molecules do not have time to block the particles of the dispersed phase at the stage of the liquid crystal structure.

Whereas the differences in the character of the change of the hardening temperature and the limiting filtration temperature are explained by the fact that the most high-melting part of the additive, as a rule, acts as the initiator of the crystallization process, causing the formation of paraffin embryos and, increasing the dispersion of the system, i.e. contributes to the depression of the limiting filtration temperature. The lower melting point molecules of the additive, concentrating in the solvation shell of the particles of the dispersed phase, prevent further splicing, and this helps to lower the pour point.

It is possible to obtain base fuel with a given pour point directly at the direct distillation units [11]. Straight-run fractions have rather low freezing and filtration temperatures.

Studies have found that to create a new type of Arctic diesel fuel DAp-53 \(-39\), light gas oil and kerosene fractions are involved. For the first time, low-fouling diesel fuel was obtained from Talakan oil. As a result of the research conducted, a new composition of Arctic diesel fuel from the oil of the Talakanskyoie field of the Sakha Republic (Yakutia) has been scientifically substantiated, which has a pour point of \(-53 \, ^{\circ} \text{C} \).

A technology to obtain an Arctic diesel fuel from the oil of the Talakanskyoie field of the Sakha Republic (Yakutia) has been developed that involves the primary distillation separating a kerosene fraction and a light atmospheric gas oil with their further compounding and injection of the Difron 315 depressant 0.55 \% by weight in an organic solvent.

At the primary distillation unit, a kerosene fraction and light atmospheric gas oil (light diesel fraction) are obtained from the Talakan oil. The fractions obtained are mixed in a certain ratio and the mixture is sent to a continuous jet mixer. From the tank (Figure 1) E-1, using a dosing pump H-1, a depressant is fed into the in-line mixer. Due to the high efficiency of the mixer, a high homogenization of the mixture occurs. The resulting diesel fraction enters the tank commercial products RVS-2. Long-term storage of diesel fuel leads to product stratification, thereby deteriorating its quality. To prevent delamination, the technology provides a circulation scheme for a commercial product. The product from the tank RVS-2 using an existing pumping pump H-2 is pumped through a jet hydraulic mixer. The SGS mixer is installed inside the tank and connected to the receiving-dispensing pipe. The design of the SGS mixer and the way it works contribute to the coverage of the entire volume of the tank.

Submerged hydraulic axisymmetric jets emerge from the nozzles. There is a continuous mass transfer between the jet and the medium, during which the mass of the jet increases. The initial flow turbulence is determined by the mixer design, while the jet propagation angle reaches the values necessary to ensure the efficiency of the jets in the entire volume of the tank [12-15].

The use of an innovative jet hydraulic mixer for mixing petroleum products provides intensive mixing of petroleum products in tanks and ensures stable quality of petroleum products during storage.

The technology makes it possible to produce winter and arctic varieties from summer diesel fuel by adding depressants.

Commodity summer diesel fuel from the tank RVS-1 pump H-3 is fed into the in-line jet mixer. Using the dosing pump H-1 from the tank E-1, the depressant is fed into the mixer. The resulting homogeneous mixture enters the tank of commercial diesel fuel RVS-2. The resulting diesel fuel is additionally mixed in the tank RVS-2 in the mixer installed on the line of the product input.
3. Conclusions
It was established that the indicators of the limiting filtration temperature and Ts characterize different physical phenomena occurring in diesel fuel and, as a result, differences in the effect of additives on lowering the limiting filtration temperature and T3 are manifested: Difron 315 additive at a concentration of 0.55% by weight has the best depressor properties, and Keroflux 6100 additive at a concentration of 0.2% by weight.

All depressant-dispersant additives withstood the tests on the sedimentation stability of a complex of properties.

As a result of the research, a technical requirement has been developed for a new generation of low-condensation diesel fuel with depressant additives and a type of new fuel has been developed: - Arctic DA-53 / -39 for use up to minus 50 °C.

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