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MOLECULAR WEIGHT DISTRIBUTION OF N-PARAFFINS IN COMPLEX FUEL MIXTURES AND THEIR EFFECT ON COMMODITY DIESEL FUELS SPECIFICATION

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A comparative analysis of the molecular weight distribution of n-paraffins in diesel fuel mixtures is made and the impact of n-paraffins on the specification of commercial diesel fuels is studied.

The effectiveness of depressant-dispersant additives is largely determined by the composition of diesel fuel (DT) and its characteristics. Fuels with various hydrocarbon compositions and qualitative characteristics have different abilities for injectivity of depressant-dispersing additives. Based on this, the interaction of the additive with diesel fuels of various fractional and group hydrocarbon composition and the effect of n-paraffins contained in the fuel were evaluated.

It has been noted more than once that diesel fuels with wide boiling ranges are more susceptible to depressant-dispersant additives than fuels of narrow fractional composition. For this reason, depressant-dispersant additives differ in sensitivity to the fractional composition of fuels [1].

Objective: to determine the optimal potential of the intermolecular distribution of n-paraffins with a chain length of C_{17} to C_{33} in diesel fuel. The detailed study of the qualitative and quantitative composition of n-paraffins contained in diesel fuels grade F and class 2, and their direct effect on the operation depressant-dispersant additive is carried out with the method of ASTM D 5442-2017. The standard method to test petroleum paraffins by gas chromatography ASTM D 5442-2017 describes the quantification and distribution of paraffins by the number of carbon atoms in the range from n-C_{17} to n-C_{44}. Based on the obtained data, graphical dependencies of the n-paraffins molecular distribution on their content and mass concentration in oil products were derived.

The high susceptibility of n-paraffins to depressants and dispersants is due to action of the additives, which interact with crystallizing paraffins. N-paraffins in fuels significantly worsen its low-temperature properties, since they have a high pour point. There is an optimum content of paraffins in the fuel in which the additive effect manifests itself best. If there are too many paraffins, then the effectiveness of any additives is reduced. Heavy paraffin hydrocarbons readily form crystal nuclei, deteriorating low-temperature properties of diesel fuel. However, they are necessary so that the depressor can be sorbed on their surface. This means that paraffins have a positive effect on the fuel injectivity to depressants and dispersants.

The solid phase released from the fuel is a high-melting hydrocarbon mainly of the paraffin series, as well as aromatic and naphthenic hydrocarbons with long side chains.

DT consists of the following n-paraffins: C_{20} –, BP 345°C
C_{21} – BP, 358°C
C_{22} – BP, 371°C
C_{23} – BP 383°C
C_{24} – BP, 394°C
C_{25} - C_{30} –MP, 53-65°C
C_{31} – C_{34} - MP, 67-72°C

In this case, the temperature lowers, and high-melting hydrocarbons primarily fall out on the crystal lattice of which hydrocarbons with a lower melting point containing a smaller number of atoms in the molecule, successively crystallize. Their growth rate depends on the cooling rate of the fuel, the intensity of mixing, viscosity and the presence of additives. The magnitude of the pour point and the cloud point are mainly dependent on the total wax content, as well as on the fuel composition and solubility. Equally important are such characteristics of paraffins as molecular weight, normal paraffinic chain length, and the molecular weight distribution.

The results of OJSC "VNII NP" research [2] showed that each DT type is characterized by an optimal content of paraffinic hydrocarbons, in which the effect of depressants appears best. Practical data: content C_{19+} about 3 % mass. (a boiling range of diesel fuel 160-370 ° C).

It was found that for each type of fuel there is its own optimal paraffin depressant-dispersant composition in which the desired effect is observed. Effect of temperature input is also important for the additive. 40-50°C is the optimum temperature.

The prototype of the study is a patent [3], which is based on the addition of a heavy component to the diesel fraction with further consideration of the effect of high-boiling paraffins on the low-temperature properties of diesel fuel and additive injection.

To conduct research, we used samples of diesel fuel and petroleum products of various fractional composition, and atmospheric gasoil and the residue of mild hydrocracking as fractions containing saturated hydrocarbons, (Table. 1, Fig. 1), and the additive of the Clariant company *(Switzerland)*.

Table 1. – Oil products quality indicators

Diesel Fuel	DT Fraction (180-300)°C	Mixed DT Fraction (180-360)°C	Atmospheric Gasoil	Mild Hydrocracking Residue
Fractional Composition				
Initial Boiling Point, °C	174	184	213	358
10%, °C	205	216	279	380
50%, °C	243	278	329	390
90%, °C	282	338	358	410
95%, °C	291	351	364	418
Final Boiling Point, °C	297	357	367	433
Total Distillation, % об	98.5			
Cloud Point, °C	-29	-7		
Limit Temperature Filterability, °C	-30	-8		

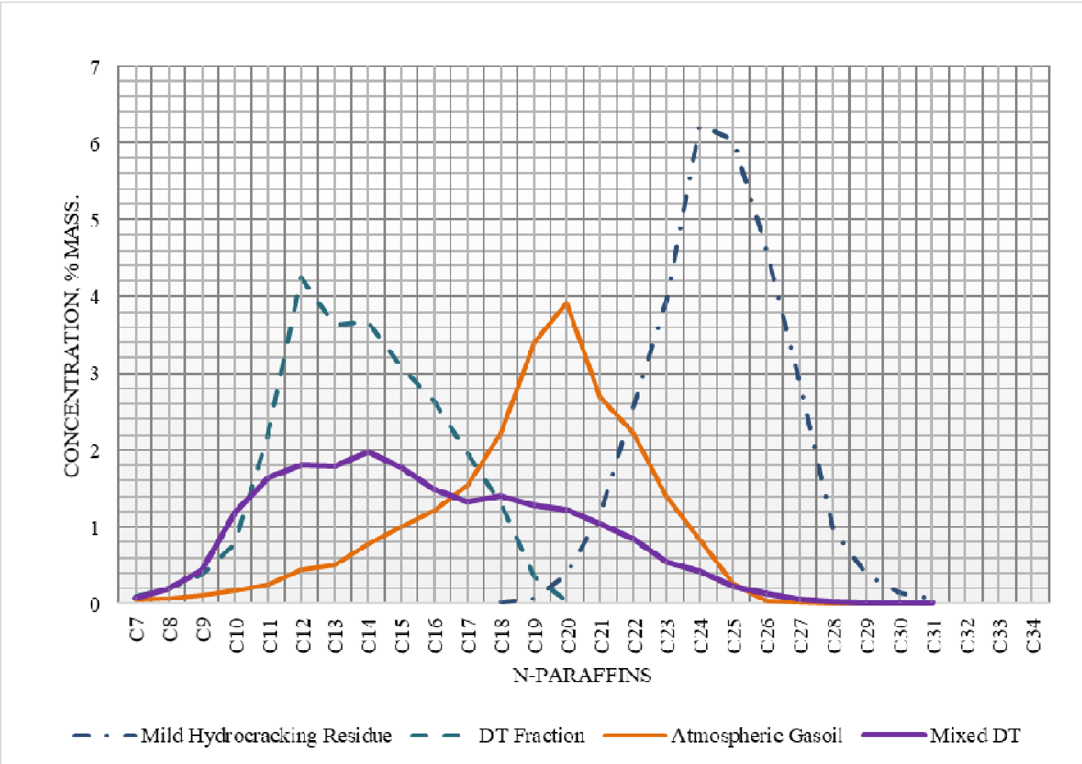

Figure 1. – Molecular weight distribution of n-paraffins in diesel fractions

With a constant amount of depressant-dispersant additive, changing only the amount of mild hydrocracking residue introduced into the diesel fraction, a significant decrease in the limiting filterability temperature and an increase in the cloud point are observed (Table 2). The greatest effect and decrease in the limiting filterability temperature is observed with the addition of 3.8% of the mass of the residue.

By varying the amount of the atmospheric gasoil, we observe the same changes of the low temperature properties. The only difference is that in this case, atmospheric gasoil consumption is much greater. The best results in terms of "limiting filterability temperature" were obtained by using the mild hydrocracking residue containing high molecular paraffin hydrocarbons.

Table 2. – Change of the low-temperature properties of diesel fuel by the amount of mild hydrocracking residue

Diesel Fuel	DT Fraction(180-300)°C					
Amount of Mild Hydrocracking Residue, % mass.	0	1.3	2.5	3.8	5	6.1
Amount of DT Fraction, % mass.	100	98.7	97.5	96.2	95	93.9
Dodiflow S-142, ppm	200	200	200	200	200	200
Limiting Filterability Temperature, °C	-30	-30	-36	-43	-22	-18
Cloud Point, °C	-29	-26	-23	-20	-16	-11
Limiting Filterability Temperature of the 20% Lower Layer, °C	-30	-29	-25	-28	-17	-18

A similar dependence of the low-temperature properties on the amount of the mild hydrocracking residue is observed for mixed DT (Table 3). In this case, we considered only the effect of adding the mild hydrocracking residue, since atmospheric gasoil is already present in the DT mixture.

Table 3. – Change of diesel fuel properties by the amount of mild hydrocracking residue and atmospheric gasoil

Diesel Fuel	DT Fraction (180-300)°C									Mixed DT Fraction (180-360)°C				
Amount of Atmospheric Gasoil, % mass.	0	1.3	2.5	3.8	4.9	6.1	7.2	8.3	9.4					
Amount of Mild Hydrocracking Residue, % mass.										0	0	0.8	1.6	2.4
Amount of DT Fraction, % mass.	100	98.7	97.5	96.2	95.1	93.9	92.8	91.7	90.6	100	100	99.2	98.4	97.6
Dodiflow S-142, ppm	200	200	200	200	200	200	200	200	200	0	600	600	600	600
Limiting Filterability Temperature, °C	-30	-30	-30	-30	-31	-32	-33	-35	-37	-8	-21	-23	-28	-33
Cloud Point, °C	-29	-28	-28	-26	-25	-24	-23	-20	-16	-7	-7	-6	-6	-5
Limiting Filterability Temperature of the Lower Layer, °C	-30	-29	-29	-29	-30	-30	-31	-31	-34		-16	-18	-25	-33

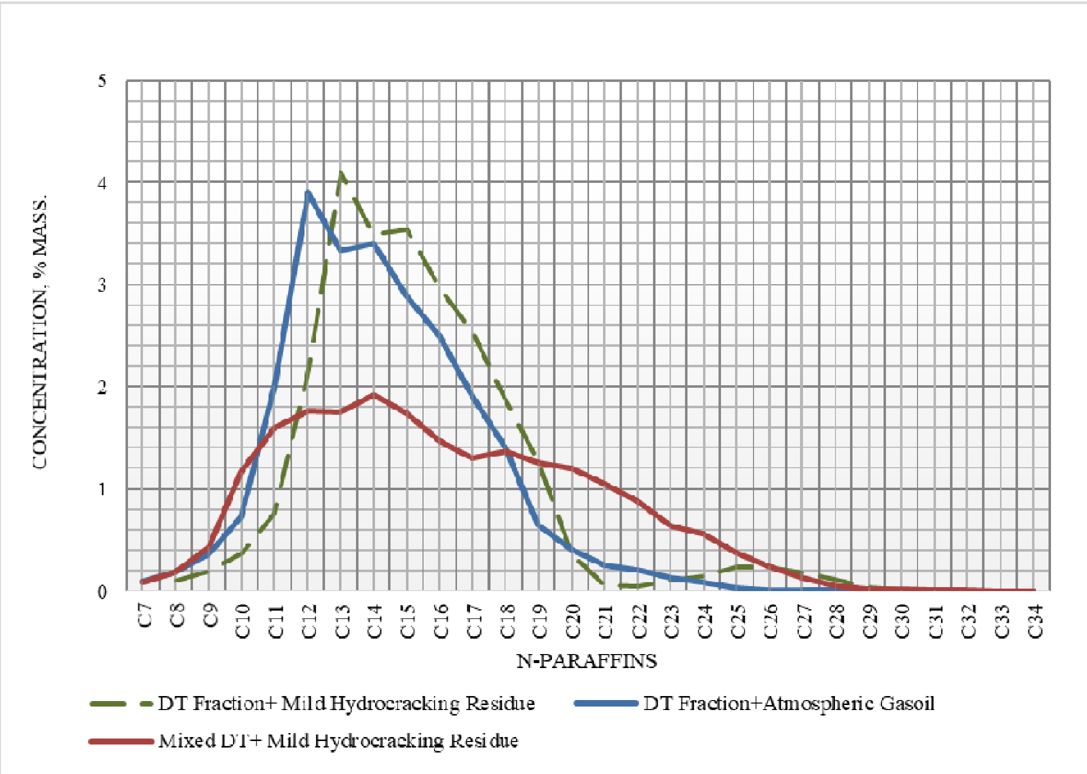

Figure 2. – Molecular weight distribution of n-paraffins in mixtures of analytes

The graph (Fig. 2) shows that paraffin hydrocarbons C23-C31 and higher provide the injectivity of additives and promote their action, thereby improving the low-temperature properties of diesel fuel. The heavier fractions of atmospheric gasoil and the mild hydrocracking residue can significantly lower the temperature of the limiting filterability temperature.

Thus, the method and systematic approach to studying the effect of n-paraffins in the composition of complex fuel mixtures allows to increase the forecast of the operation and quality characteristics of commercial fuels.

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