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Thermographic Studies of Fuel Oil in the Presence of Nikel-2 Ethylhexanoate

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Abstract

The results of thermographic studies of West Siberian crude fuel oil with the addition of nickel 2-ethylhexanoate as a catalyst are presented. The sample of fuel oil in the presence of nickel 2-ethylhexanoate practically completely turns into products evaporable under these conditions at a temperature of 454°C already, whereas fuel oil without such an additive, even at a temperature of 477° C, retains up to 20% of the initial mass.

Keywords: thermographic studies, fuel oil, destruction, catalysis, nickel 2-ethylhexanoate.

In the processes of catalytic cracking, hydrocracking, visbreaking, catalysts containing molybdenum, nickel, cobalt, tungsten and other metals are widely used [1]. These industrial processes are usually carried out using heterogeneous catalysts in the form of fixed or fluidized-bed granules or pellets. The high content of various heteroatomic, organometallic compounds and asphaltenes in raw materials makes it difficult to use the existing technologies for heavy hydrocarbon processing due to the rapid poisoning of classic catalysts. The production of catalytic systems directly in the process of heavy hydrocarbon thermal cracking is therefore of interest.

When using metal salts as additives in the processes of hydrocarbon cracking and visbreaking, the catalytic activity of these compounds is explained by the formation of metal oxides or sulphides [2,3]. According to the authors, high catalytic activity of metal salts is associated with the formation of metal sulphide or oxide ultrafine particles of about 90-100 nm or less.

The formation of metal sulphides can be explained by the fact that at temperatures above 360-370^{0}C the processes of intensive destruction of petroleum hydrocarbons, including sulphur-containing heavy hydrocarbon compounds with the production of hydrogen sulphide and mercaptans start. Simultaneously with hydrocarbon destruction, the processes of polycondensation and coke formation increase significantly at these temperatures. It is for this reason that the industrial atmospheric and vacuum distillation of crude oil is carried out at the bottom temperatures not exceeding 360-370 ° C.

The authors of the above mentioned study [2] assumed that at the beginning of the process, metal oxides are formed, which subsequently turn into sulphides. However, in the presence of hydrogen formed in the process of petroleum products thermal destruction, metal ions can be reduced to metals. This is the basis for the industrial production of catalysts, for example, nickel, cobalt supported on kieselguhr, coal and other carriers using the salts of these metals.

According to GOST 10585-99, fuel oil does not contain such chemically active compounds as hydrogen sulphide and mercaptans. Hence thermally resistant (up to 360-370^{0}C) sulphur-containing oil compounds can be the sulphur source in chemical transformations followed by the formation of new sulphur compounds. Obviously, the formation of metal sulphides is unlikely to take place at temperatures not exceeding 360-370^{0}C.

The purpose of our study was to determine the chemical transformations while heating West Siberian crude fuel oil in the presence of organic nickel salt in catalytic amounts.

Many organic metal salts decompose at temperatures below 360-370^{0}C and this does not exclude the possibility of the participation of these metals or their ions in oxidation-reduction reactions occurring in fuel oil at these temperatures. It should also be noted that the thermal effect (up to 360-370° C) on fuel oil should not lead to sulphur-containing compound destruction processes.

Experimental.

West Siberian crude fuel oil was chosen as a research object (its ratings are presented in Table 1).

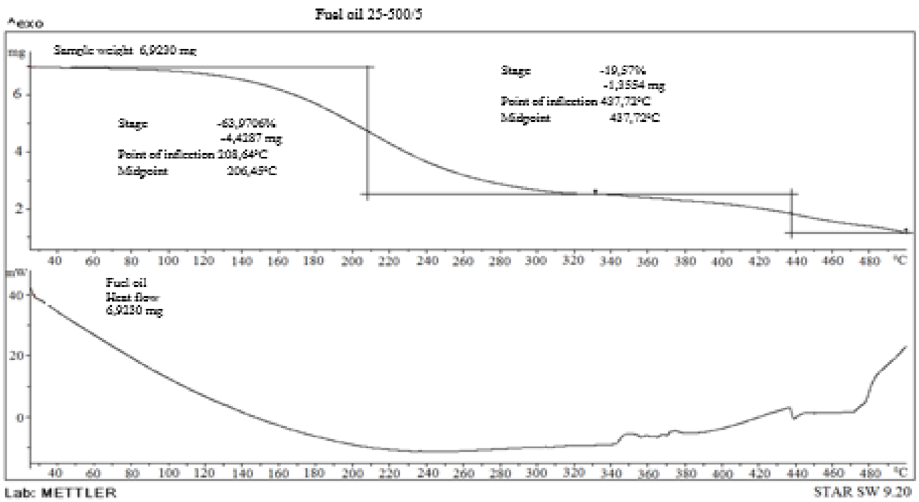
Thermographic studies were carried out using a TGA / DSCI thermal analyzer from MettlerToledo, Switzerland. Temperature range was 25 -500° C. The rate of temperature increase was 5^{0}C / min. Weighting scale resolution was 1 μg [4].

Nickel 2-ethylhexanoate produced by Chemos GmbH (Germany) was used as metal-containing additives in petroleum products.

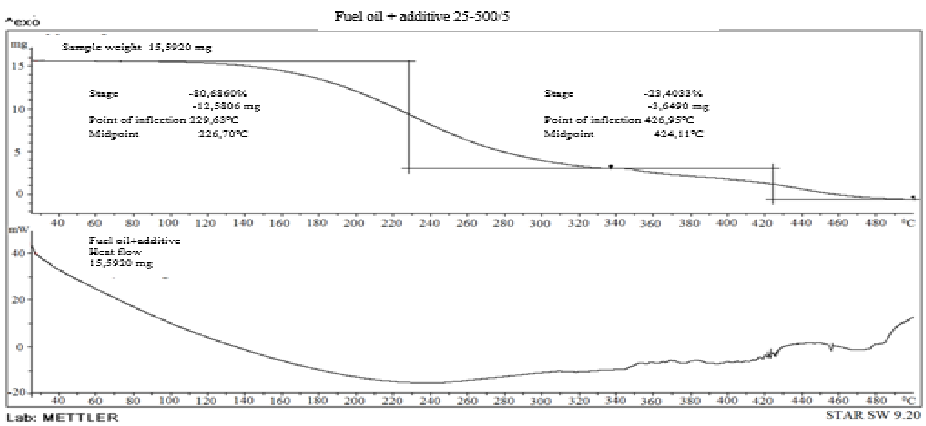
Table 1: West Siberian crude fuel oil characteristics according to GOST 10585-99 rev.1, 2

S.No.	Characteristic Name	Values		Method
		Actual	Rated	
1	Density at 100°C, kinematic, cSt, max	47,4	50,0	GOST 33
2	Ash content, % max	0,05	0,05	GOST 1461
3	Mass fraction of mechanical impurities,%, max	0,01	1,0	GOST 6370
4	Mass fraction of water,%, max	N/A	1,0	GOST 2477
5	Content of water-soluble acids and alkalis	N/A	N/A	
6	Mass fraction of sulphur,%, max	2,7	3,0	ASTM D 4294
7	Content of hydrogen sulphide and volatile mercaptans	N/A	N/A	GOST 10585
8	Open-cup flash point, ^{0}C, min	150	110	GOST 4333
9	Pour-point, ^{0}C, max	9	25	GOST 20287
10	Calorific value, kJ/kg, min	41020	39900	GOST 21261
11	Density at 20^{0}C, kg/m^3	988,0	Not rated	GOST 3900

As can be seen from the thermogram of fuel oil and of fuel oil with the addition of nickel 2-ethylhexanoate, they differ significantly (Fig. 1).



a)



b)

Figure 1: Thermogram of fuel oil sample (a) and of fuel oil sample with the addition of nickel 2-ethylhexanoate in an amount of 0.1% wt in terms of nickel (b).

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Figure 2 shows the dependence of sample weight loss on temperature. The difference in the processes occurring in fuel oil with increasing temperature is particularly distinctly seen. Some discrepancy between the curves in the initial temperature segment is explained by the difference in the initial sample weight and the measurement error.

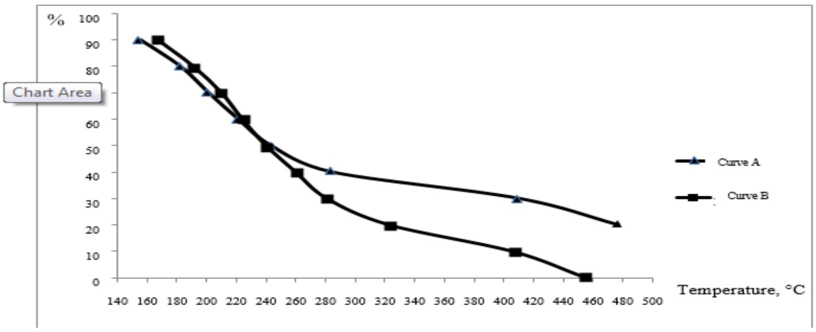

Figure 2: Mass-change of fuel oil sample (a) and of fuel oil sample with the addition of nickel 2-ethylhexanoate with increasing temperature.

It is clearly seen from the curve (Fig. 2) that the mass loss of the fuel oil sample with the addition of nickel 2-ethylhexanoate at the rate of 0.1% wt of nickel per the feedstock mass increases significantly at temperatures above 250-260^{0}C. Since such an additive cannot affect the evaporation of the hydrocarbons present in fuel oil, it has to be assumed that their destruction can be affected while heating. The content of nickel 2-ethylhexanoate is insignificant, and therefore the sample mass loss through the products of salt decomposition cannot significantly affect the results of the studies.

To determine the reasons for the impact of the addition of nickel 2-ethylhexanoate on the processes of petroleum hydrocarbon destruction, ther Curve A tudies of nickel 2-ethylhexanoate sample were carried out.

Sample 1

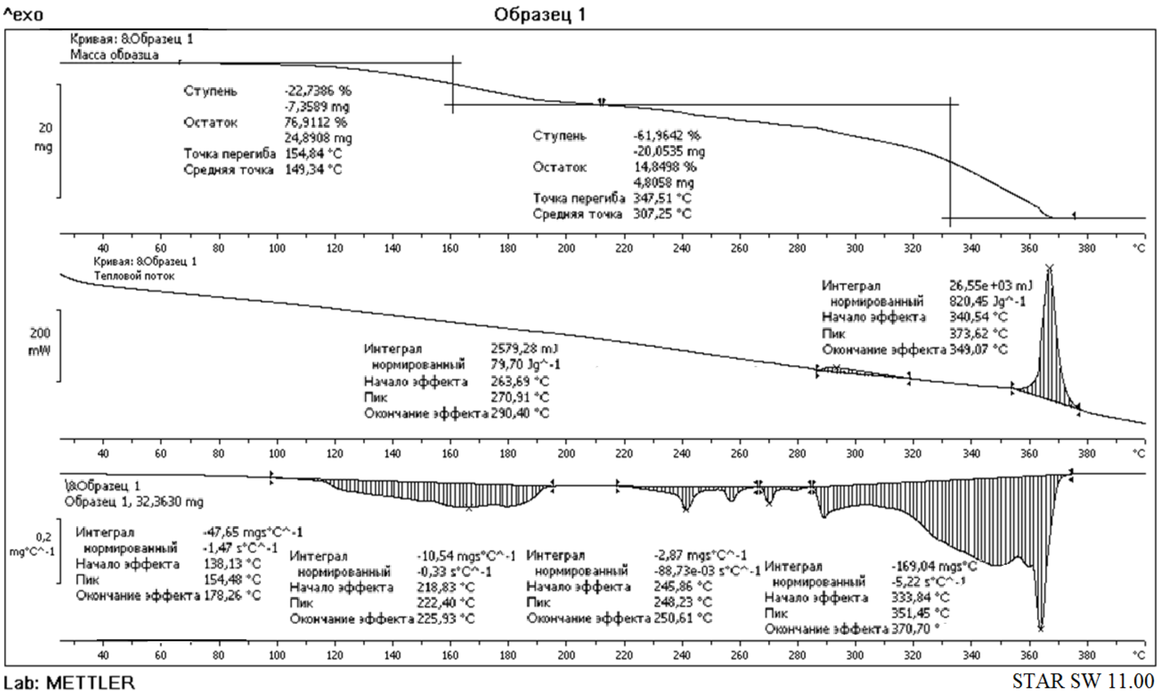

Figure 3: Nickel 2-ethylhexanoate sample thermogram.

Nickel 2-ethylhexanoate sample mass loss down to 225.93° C (Fig.3) can be explained by the evaporation of the available impurities and solvent. At a temperature of 245.86 ° C and above, nickel 2-ethylhexanoate decomposition starts. It is at these temperatures that a significant change in the dependence of sample mass loss on temperature for the fuel oil sample with the addition of nickel 2-ethylhexanoate occurs (Fig. 2).

Since, as noted above, the content of nickel 2-ethylhexanoate is low, the sample weight loss through the salt decomposition products cannot significantly affect the results of the studies.

Therefore, we can assume that catalytic destructive processes occur in the fuel oil sample containing nickel 2-ethylhexanoate at temperatures above this additive decomposition temperature.

It is likely that nickel 2-ethylhexanoate decomposition at these temperatures in the presence of petroleum hydrocarbon thermal cracking products can lead to the formation of nickel (or its new compounds), which is able to strongly influence the cracking processes. The nickel formed in the process of thermal cracking can play the role of a catalyst for hydrogenation reactions. Under such conditions, the probability of polycondensation reactions decreases; hence, a more complete conversion of fuel oil into evaporation products also becomes less probable. Thus, as shown by the results of thermographic studies (Fig. 1 and Fig. 2), West Siberian crude fuel oil can be practically completely processed into distillate and gaseous products when heated in the presence of such salts.

While destruction reactions relate to endothermic reactions, polycondensation reactions are regarded as exothermic reactions. From Fig. 1 we can see that exothermic reactions in the fuel oil under study start at temperatures above 340° C. Fig. 2 shows that at lower temperatures of the sample with the addition of nickel 2-ethylhexanoate (454^0C), a weight loss of up to 99.7% is achieved compared to the fuel oil sample without an additive at a temperature of 477^0C (80%).

Besides, the rest most probably contains nickel or its compound and we can speak about almost complete conversion of fuel oil into low-molecular products. [5,6]

The obtained results of thermographic studies indicate that the use of additives in the form of nickel 2-ethylhexanoate in fuel oil or in other heavy hydrocarbon feedstocks can deepen crude oil processing, both at the atmospheric distillation stage and in the process of heavy hydrocarbon-containing feedstock vacuum distillation, during cracking, visbreaking, delayed coking or any thermal action [7].

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CONCLUSIONS

1. Thermographic study of a fuel oil sample obtained from West Siberian crude oil in the presence of nickel 2-ethylhexanoate showed that at temperatures above the additive decomposition temperature, the rate of petroleum products evaporation is increased due to the destructive processes occurring in fuel oil.
2. The fuel oil sample with the addition of nickel 2-ethylhexanoate practically completely turns into the products evaporable under these conditions at a temperature of 454° C already, whereas the fuel oil sample without such an additive retains up to 20% of the initial mass at a temperature of 477° C.

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