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Catalytic Processes in Heavy Hydrocarbons in the Presence of Ultradispersed Nickel Suspension

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Abstract

In the process of distillation of West Siberian crude fuel oil and hydrotreated vacuum gas oil in the presence of 0.3 wt % of Nickel 2-ethylhexanoate, the catalytic effect of the formed nickel nanoparticles was established. Unlike a conventional thermal process without a catalyst, 49.6 wt % of hydrocarbons with a boiling point of up to 350^0C and 16,8 wt % with a boiling point of 350-360^0C are distilled from fuel oil. The distillation of vacuum gas oil subjected to hydrotreatment under specified conditions, allows obtaining of 37.6 wt % of hydrocarbons boiling up to 360^0C. The addition of 0.3 wt % of Nickel 2-ethylhexanoate to crude oil has no significant effect on the yield of products during distillation.

Keywords: Fuel oil, crude oil, vacuum gas oil, atmospheric distillation, aromatic, naphthenic, paraffin hydrocarbons.

In the previous papers [1-3], as a result of thermographic study of West Siberian crude fuel oil with the addition of Nickel 2-ethylhexanoate, we established that at temperatures above Nickel 2-ethylhexanoate decomposition temperature, the nature of destructive processes occurring during thermal treatment changes. A fuel oil sample with Nickel 2-ethylhexanoate added at a temperature of 454^0 C already gets almost completely converted into the products volatilizable under these conditions, while from a fuel oil sample without this additive only about 80% of the initial mass evaporates even at a temperature of 477^0. As a result of studying the samples obtained in the process of thermal treatment of fuel oil containing Nickel 2-ethylhexanoate at a temperature of up to 300^0C, by means of atomic force microscopy the formation of nickel nanoparticles was established [2,4]. Based on these results, it can be assumed that the addition of Nickel 2-ethylhexanoate to crude oil can allow us to deepen the processing of heavy hydrocarbon raw materials at the stage of atmospheric and vacuum distillations, in the processes of cracking, visbreaking, delayed coking or any thermal impact on the products containing hydrocarbons. Obviously, the conditions of the processes occurring in the process of fuel oil distillation will be significantly different from those in the fuel oil sample during thermographic study. Therefore, in this paper we have studied the impact of Nickel 2-ethylhexanoate in the process of distillation of crude oil and petroleum products.

EXPERIMENTAL

As objects of study were chosen: West Siberian crude fuel oil, specifications in accordance with GOST 10585-99 were provided in the previous study [1,2]; Nizhnevartovsk oil USN 4/1, plant No. 1 sulfur content -0,98%, vacuum gas oil (fr.350-480) of the oil specified after hydrotreatment.

Fuel oil Engler distillation was conducted in accordance with GOST 2177-99 in the PE-7510 apparatus.

Iodine number and the content of aromatic hydrocarbons were determined according to GOST 2070-82 and GOST 12329-77.

In Tables 1 and 2 the results of West Siberian crude fuel oil Engler distillation in the presence of 0.3 wt % of Nickel 2-ethylhexanoate are presented.

Table 1: Results of West Siberian crude fuel oil distillation in the presence of 0.3 wt % of Nickel 2-ethylhexanoate

Temperature, ^{0}C	295	319	328	332	336	34	344	347	349	350	352	353	358
Volume of distillate, ml	5	10	15	20	25	30	35	40	45	50	55	60	66

Table 2: Mass balance of fuel oil distillation

Name of product	Loading, g	%	Obtained	Fraction, g	% to raw material
Fuel oil +0,3 wt % catalyst	88,2	100	1.Fraction (218- 350 ^{0}C) 2.Fraction(350-360^{0}C) 3.Fraction (360^{0}C and above) 4.Losses (gas)	43,8 14,8 27,6 2,0	49,6 16,8 31,3 2,26
Total				88,2	100

To exclude any possible errors of the data evaluation, fuel oil distillation was carried out without a catalyst. In this case, only 7 ml of light fractions was distilled from 90 ml of fuel oil with a boiling point of 291-350^{0}C. In the presence of Nickel 2-ethylhexanoate, almost half of the initial fuel oil (49.6 wt %) is distilled with a boiling point of up to 350^{0}C and another 16.8 wt % - in the temperature range of 350 to 360^{0}C (Tables 1, 2). Iodine number of the fraction boiling up to 350^{0}C is 0.34, that of the 350-360^{0}C fraction is even less - 0.24g J_2/100 g. In accordance with the requirements for diesel fuels, it should not exceed 6g J2/100 g. These data are consistent with the results obtained during thermographic study [1].

It should be noted that in the course of the experiments with fuel oil, the evolution of about 2 wt % of gaseous products is observed, being indicative of the formation of minor amounts of hydrogen and light hydrocarbons or possible hydrogenation and alkylation when performing atmospheric distillation in the presence of nano-sized nickel. This suggests the catalytic C-C bond breaking with subsequent isomerization of the products under the influence of nano-sized nickel particles. In this case we are talking about the weakest bonds in petroleuml hydrocarbons. Low content of olefinic hydrocarbons in the products of distillation is indicative of the distinctive features of this process, as contrasted with conventional thermal cracking. Presumably, in the presence of nanonickel, alkylation and hydrogenation of olefins also take place.

Fuel oil is a mixture of hydrocarbons, resistant to 360-370^{0}C paraffinic, naphthenic and aromatic hydrocarbons. However, aromatic hydrocarbons having lateral weak C-C bond, conjugated with an aromatic ring, may decompose even faster than paraffin hydrocarbons. Naphthenic hydrocarbons under thermal influence are characterized by dealkylation or shortening of the paraffinic side chains. The stability of paraffinic side chains is much lower than the resistance of the ring. High molecular weight paraffinic hydrocarbons have the lowest thermal resistance. The majority of the branched paraffin hydrocarbons studied are known to be less stable in thermal relation than the corresponding paraffin hydrocarbons of normal structure. With the increasing length of side chains, the stability of these molecules decreases. Typically, the pyrolysis of paraffin hydrocarbons is accompanied by the formation of unsaturated hydrocarbons, hydrogen and saturated hydrocarbons of smaller molecular weight.

The undistilled residue (360^{0}C fraction and above) is a 31.3 wt % movable petroleum product with solid inclusions. Condensed aromatic hydrocarbons with three and more cycles (anthracene, tetracene and others) can easily enter into diene synthesis reactions, similar to butadiene, and are able to condense even at low temperatures. The possibility of such processes is implied by high boiling point of distilled products, small iodine number of fractions, the formation of solid inclusions in the residue (360^{0}C fraction and above) and small amount of gaseous products.

According to the results of thermographic study of Nickel 2-ethylhexanoate [1], it starts decomposing at a temperature of 245,86^{0}C. It is at temperatures above that when there is a significant change in the dependence of a sample mass loss from temperature for a fuel oil sample with Nickel 2-ethylhexanoate added. Therefore, the use of Nickel 2-ethylhexanoate as an additive in the process of crude oil distillation should not significantly affect the results of this distillation. On the other hand, in this case, the formation of sulfides, mercaptides or other sulfur and nickel compounds is possible, before the decomposition of Nickel 2-ethylhexanoate occurs. As is known, in the process of atmospheric distillation, the removal of active sulfur-containing compounds (hydrogen sulfide, mercaptans, etc.) from crude oil takes place, and therefore they are not found in fuel oil.

Figure 1 presents the results of crude oil distillation (sulfur content: 0.98%) in the presence of Nickel 2-ethylhexanoate without the catalyst specified.

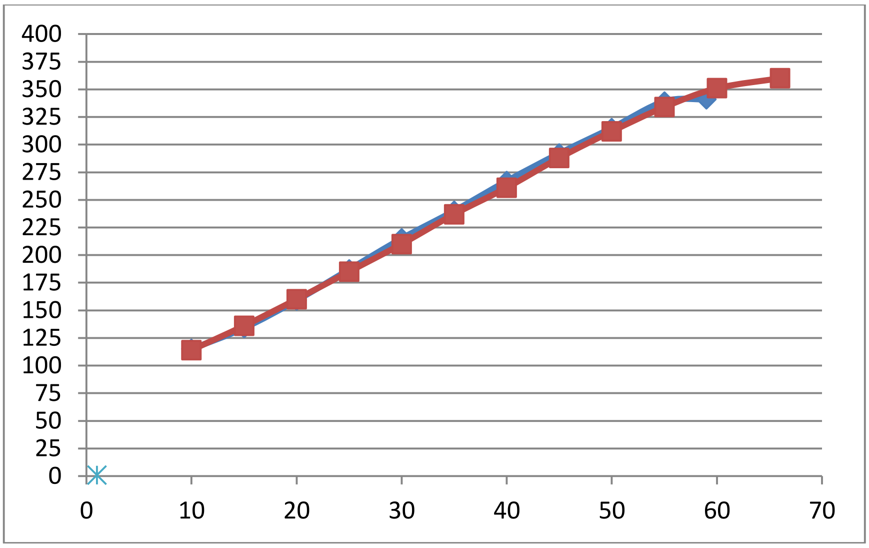

Figure 1. Results of Nizhnevartovsk crude oil distillation in the presence of 0.3 wt % of Nickel 2-ethylhexanoate and without the catalyst

According to the results of distillation (Fig.1), the presence of 0.3% wt % of Nickel 2-ethylhexanoate has no significant effect on the course of distillation. At the end of distillation (more than 50ml), when the products boiling above 330-340^{0}C are being distilled off, some increase in the fraction selection from 55.4 to 62.2% wt when using Nickel 2-ethylhexanoate is observed.

Since the distillation of crude oil was carried out up to the temperature at which hydrocarbons with a boiling point of up to 360^{0}C are stripped, but prior to thermal cracking of crude oil, temperature in the still was about 20^{0}C above. However, the presence of nickel compounds does not have such a significant impact on the distillation results, as it is the case with fuel oil. It can be assumed that the catalytic effect of Nickel 2-ethylhexanoate on the processes occurring during thermal treatment of fuel oil is caused by the formation of a metallic nickel suspension, but not sulphides. The presence of active sulfur-containing compounds in crude oil, most likely, leads to the formation of sulfides, mercaptides or other sulfur and nickel compounds and deactivates the catalytic effect of Nickel 2-ethylhexanoate or Ni^{2+} has no catalytic effect on the processes. Therefore, it can most likely be noted that the stripping of additional quantities (approximately 70 % wt) of light petroleum products (fractions boiling below 360^0C) from fuel oil as a result of ordinary distillation is only possible due to catalytic degradation of hydrocarbons.

To study the probability of the formation of nano-sized nickel in the process of distillation, vacuum gas oil after hydrotreatment was also used. The distillation of the gas oil specified in the presence of 0.3% wt of Nickel 2-ethylhexanoate allows us to strip 37.6% wt of liquid hydrocarbons with a boiling point of 228-360^0C (Tables 3,4).

Table 3: Results of distillation of vacuum gas oil obtained from West Siberian crude fuel oil after hydrotreatment in the presence of 0.3% wt of Nickel 2-ethylhexanoate

Temperature, ^{0}C	323	336	345	350	356	361
Distillate, ml	10	15	20	25	30	38

Table 4: Mass balance of vacuum gas oil distillation

Name of product	Loading, g	%	Obtained	Fraction, g	% to raw material
Vacuum gas oil + 0,3% wt of catalyst	87,8	100	1. Fraction (228-360 ^{0}C) 2. Fraction (360^0C and above) 3. Losses (gas)	33,0 54,7 0,1	37,6 62,3 0,11
Total				87,8	100

Low amount of the produced gaseous hydrocarbons (with losses of 0.11% wt) is indicative of an insignificant amount of the products characteristic of thermal degradation. During the course of distillation, temperature in the still did not exceed 370-380^0C.

As is known, fuel oil subjected to vacuum distillation is briefly heated in tubular furnaces to 420-425^0C to prevent thermal cracking and coking. After vacuum distillation, gas oil is subjected to hydrotreatment, resulting in a significant increase in its thermal stability. Therefore, the yield of products boiling up to 360^0C during this gas oil distillation in the presence of 0.3% wt of Nickel 2-ethylhexanoate is significantly lower (37.6% wt) than it is in the case of fuel oil distillation. This is evidenced by the results of the fraction analysis for the content of aromatic hydrocarbons. The 228-350^0C fraction contains 35.5 % wt of aromatic hydrocarbons, and the 350-360^{0}C fraction - 41,2% wt. However, the distillate (particularly, the fraction boiling up to 350^{0}C) contains less thermally stable paraffinic and naphthenic hydrocarbons. It can also be assumed that the produced low molecular weight unsaturated compounds may enter into diene synthesis or alkylation reaction. Low amount of gaseous products (less than 0,11% wt) is indicative of that.

Photon correlation spectroscopy method using the Photocor Complex spectrometer has shown that the sample obtained by boiling vacuum gas oil containing 0.3% wt of Nickel 2-ethylhexanoate, is a suspension with a particle size of about 10 nm. It was also established that when boiling vacuum gas oil in the presence of Nickel 2-ethylhexanoate for a longer period of time, a metallic coating of nickel is formed on the entire surface of the bulb (like it is the case in the silver mirror reaction). These results allow us to assert a catalytic effect of nano-sized nickel suspension on the processes of vacuum gas oil degradation and its large catalytically active surface.

CONCLUSIONS

1. In the process of distillation of West Siberian crude fuel oil containing 0.3% wt of Nickel 2-ethylhexanoate, a 66,4% wt hydrocarbon fraction is formed with a boiling point of up to 360^{0}C. The distillation of vacuum gas oil, subjected to hydrotreatment, under specified conditions allows us to obtain 37.6% wt of hydrocarbons boiling up to 360^{0}C. High yield of light fractions, low content of olefinic hydrocarbons and a small amount of gaseous compounds in the distillation products are indicative of catalytic nature of the process.
2. A preliminary addition of 0.3% wt of Nickel 2-ethylhexanoate to crude oil has no significant effect on the process of distillation. Probably, the presence of sulfur containing compounds in crude oil results in the formation of catalytically inactive sulfides, mercaptides or other sulfur and nickel compounds.

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