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COMPARING PHYSICO-CHEMICAL PROPERTIES OF OIL FIELDS OF NIGERIA AND UKRAINE

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Abstract. The problem of crude oil deficit for Ukrainian refineries has been considered. To solve this problem the import of crude from Nigeria has been proposed. Physico-chemical properties of Nigerian oils, namely their fractional composition, potential yield of light fractions were investigated and compared with physico-chemical characteristics of Ukrainian crude oils. The possibility of Nigerian oils processing at JSC "Ukrtatnafta" (Ukraine) was grounded.

Keywords: Nigeria, petroleum refining, physico-chemical properties, crude oil.

1. Introduction

Modern oil-refining industry of Ukraine involves six refineries with a total capacity of above 59 mln. tons of oil per year. The largest refineries are situated in Kremechuk, Lisichansk and Kherson.

To date the oil-refining industry of Ukraine considerably depends on import. The country has enough refineries but deficit of crude. After the "record" in 1972 (14.5 mln. tons of oil and gas condensate) oil production is steadily decreased. Recently the oil production was 3 mln. t/year (8% of total capacity or 1/5 of home market demands).

The reasons of oil production decrease are:

– reserve depletion;

– decrease in capacity and efficiency of production drilling;

– deterioration of reserves structure (for a long period the reserves with an easiest access were extracted);

– sharp reduction of exploration. For recent 15 years no new great or medium field (with reserves of more than 10 mln. tons) was opened; the proven oil fields have insignificant reserves.

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Therefore, the problem of involving additional quantity of crude oil suitable to produce high-quality products is very urgent [1-2]. One of the ways to solve this problem is import of oil from Nigeria.

Nowadays Nigeria is one the most important producers of light low-sulphuric crude oil. The country ranks the twelfth place in the world to supply crude oil; its oil production is 1.9 mln. barrels per day [3]. Confirmed reserves of Nigerian oil are about 35.5 bln. barrels (almost 4.8 bln. tons). The daily production may be at the level of 3.0 mln. barrels (150 mln. tons per year). There are 159 oil fields in Nigeria, including a continental shelf and the delta of Niger river. Nigeria produces several types of high-quality oil: Forcados, Escravos, Odude and Bonny.

The country has only four refineries, but even working at full capacity, they can meet just a quarter of fuel demand in Nigeria. Aircraft and ground transport suffer from lack of fuel.

The aim of the present work is to establish the possibility of processing the Nigerian crude oil at Ukrainian refineries by comparing physico-chemical characteristics of the oil fields of Ukraine and Nigeria.

2. Experimental

Crude oils from oil fields of Nigeria which are used to produce Brent Dated and Bonny Light commercial oils (denoted as Nigeria 1 and Nigeria 2) were compared with oils from East-Ukrainian and West-Ukrainian oil fields which are used at Ukrainian refineries. The investigations were carried out in the laboratory of JSC "Ukrtatnafta" and chemmotological centre of National Aviation University.

The most interesting for evaluation are the content of high-quality oil component, their physico-chemical and operational characteristics which provide the quality of resulting products. The main indices of physico-chemical properties were determined using standard methods for oil and petroleum products [4-12].

Fractional composition was studied according to ASTM D 86-16a [13] (Table 3), ASTM D 1160 [14] (Table 4) and method which is an analog to

ASTM D 2887, ASTM D 5307 and ASTM D 6352 [15-17]. Gas chromatograph HP 7890 was used to analyze light fractions (b.b.–623 K) with a flame ionization detector and Simdis software.

To determine the metals in crude oils Varian AA240 atom-absorption spectrometer was used [18].

Density is one of the main characteristics allowing to evaluate tentatively the chemical and fractional oil composition. Depending on this index crude oils are classified as light, medium and heavy oils [1]. The light crude oils contain more gasoline fractions and less resins and sulfur. High-quality oils are produced from this type of crude. For heavy crudes with high content of resins the special treatment methods are necessary: selective treatment by solvents, adsorbents, *etc*. However, heavy crudes are the best raw materials to produce bitumen. One can see from Table 1 that Nigeria 1 oil belongs to light crudes ($r_{15}^{15} \le 0.828$), Nigeria 2 oil – to medium crudes ($r_{15}^{15} \le 0.828-0.884$).

Sulfur content is one of the important technological characteristics. Depending on this value oils are classified into three classes: 1st class – low-sulfuric oils with sulfur content from 0 to 0.5 %; 2nd class – sulfuric oils with sulfur content of 0.51–1.9 %; 3rd class – high-sulfuric oils with sulfur content above 1.9 % [1]. The investigated Nigerian oils are low-sulfuric ones of the 1st class (0.37 and 0.18 % of sulfur, respectively). The East-Ukrainian oil belongs to the 2nd class; West-Ukrainian – to the 1st class.

The presence of sulfuric compounds (hydrogen sulfide, elemental sulfur, sour sulfur and others) is undesirable because they reduce the products quality, cause the corrosion and pollute the atmosphere while fuel burning. Sulfuric compounds poison the expensive catalysts of oil processing and create ecological problems. But if sulfur content in the resulting products is higher or lower than that in the corresponding oil, this oil should be included to the higher or lower classes. So, we determined sulfur content for every narrow fraction (Table 2).

3. Results and Discussion

Physico-chemical characteristics of the investigated oils are presented in Table 1.

The sulfur contents for Nigerian and Ukrainian oils are commensurable. In the jet-engine fractions it is the same for Nigeria 1 and East-Ukrainian oils; sulfur content for Nigeria 2 is some lower than for West-Ukrainian oils. In the diesel oil fractions of both Nigerian crude oils the sulfur content is lower compared with Ukrainian oils. In vacuum distillates of Nigerian oils the sulfur content is lower in comparison with Ukrainian oils, so the operation conditions of catalytic cracking unit at JSC "Ukrtatnafta" will be improved.

According to the yield of fractions to 623 K all oils belong to the first type [1].

Water content in Nigeria 2 oil is low (0.3 wt %) and water is absent in Nigeria 1. It means that oils are easy to be transported and prepared for processing. Content of salts in them range from 2.9 to 22 mg/l.

Freezing point of Nigerian oils is considerably lower than that of West-Ukrainian oils and higher than the freezing point of East-Ukrainian oils. The content of sulfuric-acid resins is lower for Nigerian oils. Engler viscosities of all oils are commensurable. Yields of gasoline and diesel oil fractions are commensurable as well.

Table 3 represents fractional composition of oils investigated according to ASTM D 86-16a.

Table 1

Characteristics of crude oils

Index	Nigeria 1	Nigeria 2	East-Ukrainian	West-Ukrainian
Weight percentage of water, wt %	–	0.30	0.03	0.25
Salts content, mg/dm^3	2.9	21.9	8.2	40.8
Density at 293 K, kg/m^3	806.8	844.0	844.7	846.6
Weight percentage of sulfur, wt %	0.37	0.18	0.87	0.43
Weight percentage of sour sulfur, wt %	0.0097	0.0023	0.0012	0.0005
Freezing point, K	255	273	244	286
Sulfuric-acid resins content, wt %	8	14	29	20
Acidity, mg KOH per 100 cm^3	1.77	4.92	1.33	3.88
Engler viscosity at 323 K, °E	1.1	1.45	1.2	1.3
Content of dissoluble gases, wt %	0.26	0.33	0.35	0.51
Yield of gasoline fraction to 453 K, wt %	37.0	19.5	29.5	22.0
Yield of fractions to 633 K, wt %	72.0	57.3	59.0	54.5

Table 2

Sulfur content in narrow fractions of the investigated oils (wt %)

Fraction	Nigeria 1	Nigeria 2	East-Ukrainian	West-Ukrainian
IBP–335 K	0.022	0.018	0.005	0.003
335–358 K	0.021	0.004	0.007	0.005
358–378 K	0.019	0.005	0.006	0.002
378–393 K	0.027	0.012	0.006	0.004
393–413 K	0.035	0.018	0.009	0.005
413–433 K	0.046	0.019	0.018	0.011
433–453 K	0.046	0.019	0.035	0.020
453–473 K	0.060	0.024	0.057	0.034
473–493 K	0.055	0.039	0.079	0.049
493–513 K	0.108	0.047	0.110	0.072
513–533 K	0.218	0.058	0.205	0.105
533–553 K	0.362	0.070	0.385	0.184
553–573 K	0.387	0.081	0.517	0.238
573–613 K	0.446	0.130	0.674	0.362
613–633 K	0.636	0.182	0.867	0.430
633–643 K	0.654	0.210	0.942	0.437
Residuum	0.974	0.317	1.833	0.810
Vacuum distillate (residual oil vacuum distillation using ARN-2)	0.716	0.212	1.089	0.501
Residuum after residual oil vacuum distillation using ARN-2	1.217	0.428	2.409	1.142

Table 3

Fractional composition of investigated oils (IBP–633 K, vol %)

Temperature, K	Nigeria 1	Nigeria 2	East-Ukrainian	West-Ukrainian
Initial boiling point	323	331	324	330
353	7.5	3.0	5.5	4.0
373	12.0	4.0	11.5	7.0
393	18.0	6.5	18.0	10.0
413	26.0	10.0	23.0	14.0
433	30.5	14.0	27.5	18.0
453	35.0	18.5	31.0	22.0
473	40.0	22.5	34.5	26.0
493	44.5	27.0	38.0	29.0
513	49.0	31.0	41.0	32.5
533	53.0	35.0	45.0	36.0
553	57.5	39.0	49.0	40.0
573	61.5	44.0	53.0	44.5
593	65.5	48.5	56.0	49.0
613	69.0	53.0	60.0	54.0
623	70.5	56.0	62.5	56.0
633	72.5	58.0	65.0	57.0

Table 4

Fractional composition of investigated oils (fraction > 643 K, vol %)

Temperature, K	Nigeria 1	Nigeria 2	East-Ukrainian	West-Ukrainian
Initial boiling point	643	653	643	646
693	18.4	7.3	12.7	17.2
703	23.9	15.4	17.0	22.6
713	30.5	22.1	21.1	27.5
723	36.0	28.4	25.9	32.1
733	41.2	34.0	30.1	36.5
743	46.0	39.0	34.3	40.8
753	50.8	43.6	38.3	44.8
763	54.7	47.8	41.6	52.1
773	58.6	51.7	43.7	56.0
783	62.2	55.5	46.8	57.5

Table 5

Total yield (wt %) of the fractions (TBP)

Temperature, K	Nigeria 1	Nigeria 2	East-Ukrainian	West-Ukrainian
< 342	**2.8**	**2.6**	**1.7**	**1.4**
353	8.0	4.4	6.0	3.5
363	12.0	5.9	9.5	5.5
373	15.0	7.3	12.5	8.0
383	18.0	8.6	15.5	10.0
393	21.0	10.0	18.0	11.5
403	23.0	11.5	20.0	13.0
413	26.0	13.1	22.0	14.5
423	29.0	14.8	24.0	16.5
433	32.0	16.4	26.0	18.5
443	34.5	17.9	28.0	20.0
453	**37.0**	**19.5**	**29.5**	**22.0**
463	39.5	21.2	31.0	23.5
473	42.0	22.7	32.5	25.0
483	44.0	24.4	34.0	26.5
493	46.5	26.3	36.0	28.0
503	48.5	28.0	37.5	29.5
513	50.5	30.1	39.0	31.5
523	53.0	31.9	41.0	33.5
533	55.0	33.8	42.5	35.5
543	57.0	36.0	44.5	37.0
553	59.0	38.4	46.0	39.0
563	61.0	40.7	48.0	41.0
573	62.5	42.8	49.5	43.0
583	64.0	45.0	51.0	45.0
593	66.0	47.7	53.0	47.5
603	67.5	50.3	54.5	49.0
613	69.0	52.9	56.0	51.0
623	71.0	55.0	57.5	53.0
633	**72.0**	**57.3**	**59.0**	**54.5**
643	73.5	58.8	60.5	56.5
653	75.0	60.3	62.0	58.0
663	76.5	62.3	63.5	60.0
673	78.0	63.8	65.0	62.0
683	79.0	64.3	66.5	64.0
693	80.5	65.3	68.0	65.5
703	82.0	67.8	69.5	68.0
713	83.5	70.3	71.0	70.0
723	85.0	73.0	72.5	72.0
733	86.0	75.0	74.0	73.5
743	87.5	77.0	75.5	75.5
753	88.5	79.0	76.5	77.5
763	90.0	80.5	78.0	79.0
773	**91.0**	**82.0**	**79.0**	**80.5**
783	92.0	84.0	80.5	82.0
793	93.5	85.0	81.5	83.0
803	95.0	86.0	83.0	85.0
813	95.6	86.7	83.5	85.7
Residue >813 K	4.4	13.3	16.5	14.3

The total yield of the fractions of investigated oils is represented in Table 5.

The residual oil (> 643 K) was distilled according to ASTM D 1160, the results are presented in Table 4.

According to the results of atmospheric distillation Nigeria 1 is a light oil with IBP 323 K. Nigeria 2 is a heavier oil with IBP of 331 K. For Nigeria 1 37 wt % of the fractions are boiled to 453 K; for Nigeria 2 – 19.5 %. These values indicate the potential content of gasoline fractions and are commensurable with those for Ukrainian oils (29.5 and 22 wt % for East- and West-Ukrainian oils, respectively). The potential content (wt %) of diesel oil fractions: Nigeria 1 – 35; Nigeria 2 – 37.8; East-Ukrainian – 29.5; West-Ukrainian – 32.5. The yield of jet-engine fractions of Nigeria 1 and 2 oils is 24.5 and 17.0 wt %, respectively, that is essentially higher than the analogous yield of Ukrainian oils. The yield of wide oil fractions 633–813 K is 23.6 and 29.4 wt % for Nigerian oils, respectively; 24.5 and 31.2 wt % for Ukrainian oils, respectively.

Microelemental composition of crude oil is an important characteristic providing geologic-geochemical information about oil age, ways of its migration and accumulation. There are about 60 microelements in the crude oil [19-22].

Metals in crude oil considerably affect the oil processing, including catalysts poisoning, equipment corrosion and ingress into resulting products. It is known that metals concentration in crude oils varies within wide range and their average values are reduced from $n \cdot 10^{-3}$ to $n \cdot 10^{-8}$ wt % in the series: V, Fe, Ca, Ni, Na, K, Mg, Al, Hg, Zn, Mo, Cr, Cu, Co, Mn, Ba, Ge, Ag, Hf, Pb, Au, Be, Ti, Sn.

Moreover, metal content is regulated by technological regulations, namely Cu content – for raw material (gasoline fractions) of reforming, isomerization, *etc.*; V, Ni and Fe content – for raw material (vacuum gas oils and residues) of catalytic cracking and hydrofining.

Metals are mostly concentrated in resinous-asphaltenic compounds (RAC) of crude oil. Vanadium in the form of vanadyl-porphyrin complexes in the amount of 10^{-5}–10^{-2} % is concentrated in RAC being the cause of equipment strong corrosion and environment poisoning due to the formation of vanadium oxide while residuum burning. Vanadium content (ppm) in Nigeria 1 oil is 0.24; Nigeria 2 – 1.28; West-Ukrainian – 1.91 and East-Ukrainian – almost 11 (Table 6). The amount of vanadium is associated with sulfuric compounds, because vanadium promotes the sulfates reduction to hydrogen sulfide and sulfur. Thus, East-Ukrainian oil has the maximum amount of vanadium and sulfur (11 ppm and 0.87 %, respectively).

Nickel is also concentrated in RAC in the amount of 10^{-4}–10^{-3} % but in a small amount it is also presented in oil fractions of heavy oil. The same as vanadium, nickel is in the form of vanadyl-porphyrin complexes. Its amount in Nigeria 1 and 2 is 0.18 and 3.18 ppm, respectively; in East- and West-Ukrainian oils – 10.99 and 3.67 ppm, respectively.

Iron is presented in crude oils in a small amount. It is distributed within the whole range of boiling temperatures. The nature of iron compounds is studied insufficiently but it is expected that Fe is also in the form of porphyrin complexes. The highest amount of iron (41.35 ppm) was found to be in East-Ukrainian oil. In other samples its amount is relatively low (2.96, 1.3 and 4.6 ppm).

Table 6

Metals content in the investigated oils (mg/kg)

Metal	Nigeria 1	Nigeria 2	East-Ukrainian	West-Ukrainian
Iron	2.96	1.3	41.35	4.6
Zinc	0.72	0.38	4.21	1.79
Nickel	0.18	3.18	10.9	3.67
Vanadium	0.24	1.28	10.99	1.91
Copper	4.73	0.08	0.59	0.1
Manganese	not detected	not detected	0.13	0.21
Chrome	not detected	not detected	0.22	0.07
Calcium	6.52	5.07	1.64	7.47
Magnesium	2.05	1.27	1.17	5.91
Sodium	5.77	6.05	10.14	58.49
Potassium	0.63	0.36	0.43	0.92
Cobalt	0.15	not detected	not detected	not detected
Lead	not detected	0.1	0.59	not detected
Barium	not detected	not detected	0.25	14.6
Molybdenum	0.02	0.841	0.11	trace
Aluminium	not detected	2.346	6.44	3.42
Silicium	0.24	5.752	1.48	0.25

The share of alkali and alkaline earth metals (sodium, potassium, magnesium, calcium) is 10^{-3}–10^{-4} %. These elements are part of stratal water. Even the most careful treating is not able to purify crude oil from the mentioned microimpurities. All alkali and alkaline earth metals in the form of petroleum acid salts, phenolates, thiophenolates, *etc*. are present in all fractions. Among all alkaline earth metals, which were found in the studied oils, sodium has the highest share. Its concentration in West-Ukrainian oil is 58.49 ppm, in East-Ukrainain – almost 6 times less (10.14 ppm). In Nigerian oils sodium is present in small amounts – 5.77 and 6.05 ppm. The content of calcium in the Nigerian oils is commensurable with East-Ukrainian oils (5–7 ppm); its smallest content is in West-Ukrainian oil (1.64 ppm). Potassium content is insignificant in all investigated samples – less than 1 ppm. Copper is presented in all samples, the highest amount – in Nigeria 1. In other oils copper content is less than 1 ppm.

4. Conclusions

Two Nigerian crude oils were compared with the mixtures of East-Ukrainian and West-Ukrainian oils. We found the similarity of oils by their fractional composition but the yield of gasoline and diesel oil fractions of Nigeria 1 is considerably higher than those values of other oils. Nigerian oils are low-sulfuric oils, having a low freezing point and low content of sulfuric-acid resins. The yield of jet-engine fractions from Nigeria oils is considerably higher than that from Ukrainian oils; the yield of oil fractions is commensurable. The content of vanadium, iron, nickel and sodium in Nigerian oils is essentially higher than in Ukrainian oils.

On the basis of data about fractional composition, content of sulfuric compounds and sulfuric-acid resins, freezing point, viscosity, content of heavy metals we may assert that Nigerian oils Brent Dated and Bonny Light may be processed at JSC “Ukrtatnafta” without any changes in the process flowsheet and regimes.

The physico-chemical analysis of Nigerian oils allows to propose the scheme of oil processing for Nigerian refineries.

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ПОРІВНЯННЯ ФІЗИКО-ХІМІЧНИХ ВЛАСТИВОСТЕЙ НАФТ РОДОВИЩ НІГЕРІЇ ТА УКРАЇНИ

Анотація. *В статті розглянута проблема нестачі нафти для нафтопереробних заводів України. Одним з виходів з даної ситуації пропонується імпортування нафти з Нігерії. Наведені результати із дослідження фізико-хімічних показників нігерійських нафт, їх фракційної розгонки, потенційного виходу світлих фракцій; отримані дані порівнюються з фізико-хімічними характеристиками нафт східно- та західно-українських родовищ. Обгрунтована можливість перероблення нігерійських нафт на ПАТ «Укртатнафта» (Україна).*

Ключові слова: *Нігерія, нафтоперероблення, фізико-хімічні показники, нафта.*