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TEMPERATURE AND WATER EFFECT ON THE OXIDATIVE DESULPHURIZATION OF STRAIGHT-RUN DIESEL FRACTION WITH A HIGH SULPHUR CONTENT

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Abstract. The effect of temperature and water:raw material ratio on the oxidative desulphurization of straight-run diesel fraction 553–623 K has been examined. The optimum values of temperature and diesel fuel:water ratio for the raw material containing 0.87 wt % of sulphuric compounds have been determined.

Key words: desulphurization, diesel fuel, oxidative desulphurization, sulphur, sulphoxides, sulphones.

1. Introduction

The increasing demands for fuel ecological properties are the reason for the decrease of permissible amount of sulphuric compounds. At the same time the removal of sulphuric compounds (hydrofining) is the only one widely used industrial technology, which has a number of shortcomings:

• application of complicated equipment and purified hydrogen which is of short supply;

• removal of heteroatomic products and a part of aromatic hydrocarbons together with sulphuric compounds, resulting in the amount decrease of the products able to sorb over metal surfaces and lubricate them;

• impossibility of some thiophene derivatives removal.

All above-mentioned shortcomings require the development of novel technologies of oil fractions treatment, *e.g.* oxidative desulphurization. The essence of the method is the oxidation of sulphuric compounds to sulphones, sulphoxides and perhaps, sulphoacids with expressive polar properties. Such properties allow to separate them from other compounds using adsorption or extraction. Moreover, taking into account that sulphoxides, sulphones and sulphoacids have higher boiling temperatures compared with initial sulphuric compounds, they may be removed by usual distillation.

The known oxidative processes may be divided into three groups:

• technology aimed at fuel sweetening;

• processes with the aim of sulphoxides and sulphones obtaining;

• technology aimed at the decrease of total sulphur content.

The majority of works concerning the latter direction is aimed at the decrease of sulphur content to 5–15 ppm in hydrofined fuels. At the same time the application of oxidative desulphurization for straight-run fractions allows to decrease sulphur amount by less than 80 %. Therefore it is impossible to produce fuel which meets the European standards (the sulphur content is 0.0005–0.0015 mas %) from the raw material with the sulphur content more than 0.01 mas %.

To date in Ukraine it is permitted to produce diesel fuels with the sulphur content prior to 0.2 mas %. Such sulphur content may be achieved using oxidative desulphurization. Moreover such fuel has better lubricating properties and oxidation products (sulphuric concentrated compounds) may be used as lubricating fluids with a cost price higher by 10-20 % than the price of commercial diesel fuels [1]. Thus, oxidative desulphurization of straight-run diesel fuels is attractive and perspective process from the point of view of diesel fuel production with the sulphur content prior to 0.2 %, as well as of lubricating properties improvement and obtaining of sulphuric concentrated compounds.

It has been shown earlier [2] that using wide straight-run diesel fraction (WDF) with the high sulphur content (0.67 mas %) it is necessary to desulphurize at least two parts of WDF – the "head" fraction (start boiling point–553 K) and the "tail" fraction (553–623 K). Since the "tail" fraction is heavier than the "head" one, the oxidation degree is less and it is necessary to use the combination of several methods (*e.g.* rectification and adsorption) to remove the oxidation products. At the same

time the combination of two methods is a bulky and long process.

On the other hand (Table 1), the tendency of factors effect on the process proceeding is preserved without regard to any methods of oxidation products removal or combination of the methods. It means that we can use rectification only in order to simplify the technique of laboratory experiments and decrease their duration.

Since it has been shown in [1-2] that the presence of water may increase the selectivity of sulphuric compounds oxidation, it was necessary to establish the dependence of process characteristics upon its main factors – temperature and raw material:water ratio.

2. Experimental

Raw material with boiling temperatures ranging from 553 to 623 K obtained from WDF with the sulphur content 0.67 mas % has been used for the investigations. The characteristics of raw material are represented in Table 2.

The fraction oxidation was studied at high temperatures and pressure using enlarged laboratory plant, the scheme of which is represented in [3]. The experimental technique and plant description are presented in [1-3]. After oxidation the water phase was separated and oxidated straight-run fraction (oxidate) was divided and analyzed by the following scheme (Fig. 1).

The raw material and oxidation products were analyzed using standard methods for determination of total sulphur content [4], soluble gums content [5] and acidity [6].

Air was used for the oxidation of initial fraction. Raw material:air ratio, as well as process time were sustained constant during oxidation.

In order to determine the optimum pressure the strippant part was calculated at different pressures and maximum temperature of previous investigations (513 K) both in the presence of water and without it.

The amount of raw material vapors from the reactor is determined by the formula:

$$G = (g_{air} \cdot P_{svp} \cdot M)/(P - P_{svp})/29 \qquad (1)$$

where M is the molecular mass of vapors mixture of straight-run diesel fraction and water; g_{air} is the amount of air which passes throughout the reactor, kg; P_{svp} is saturation vapor pressure for the mixture of straight-run diesel fraction and water (when it is present), Pa; P is a general pressure in the reactor, Pa; 29 is the molecular mass of air.

According to (1) the graphic dependence of the amount of strippant vapors with air upon general pressure in the reactor (Fig. 2) at 513 K was plotted. One can see from Fig. 2 that at 513 K and pressures up to 3 MPa in the presence of water the strippant part is relatively large, resulting in possible considerable losses of straight-run fraction with air. The increase of pressure in the reactor over 3 MPa does not affect the decrease of strippant part. In connection with this fact, the used air after the reactor passed through a cooling condenser and cooled to 313 K in order to decrease the losses. Due to such cooling the part of straight-run diesel fraction vapors condensed and returned back to the reactor. In accordance with analogous calculations the part of strippant with air will not exceed

Table 1

Effect of oxidate liquid phase separation methods on the sulphur content in the refined fuel changing process factor

Oxidate liquid phase separation method	Content of total sulphur in the refined fuel, mas %		
	at temperatures		
	453 K	473 K	553 K
Distillation	0.65	0.61	0.68
Adsorption	0.64	0.59	0.63
Distillation-adsorption-distillation	0.29	0.24	0.35
	With/without water		
	Without water	With water	
Distillation	0.65	0.65	
Adsorption	0.64	0.63	
Distillation-adsorption-distillation	0.29	0.26	

Table 2

Characteristics of initial fractions

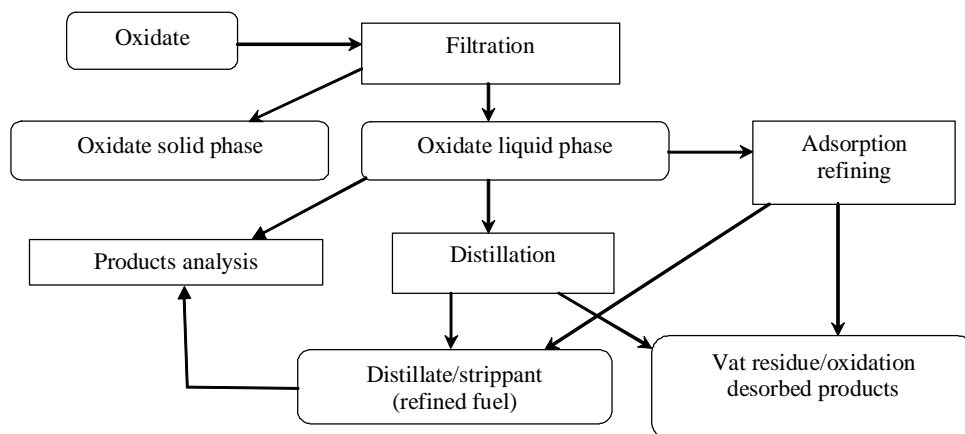| Index	Value
Density at 293 K, kg/m^3	856
Content of total sulphur, mas %	0.87
Concentration of soluble gums, mg/100 cm^3	15.0
Yield, mas % to calculate for wide straight-run diesel fraction	35.3

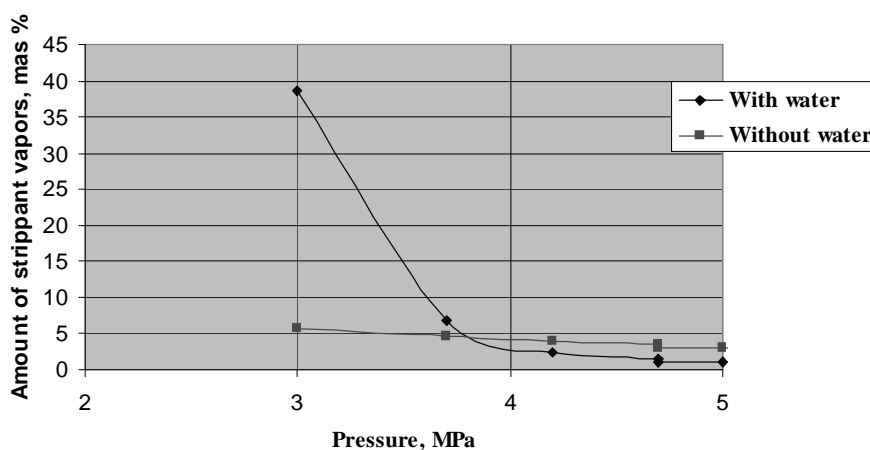**Fig. 1.** Scheme of oxidate division and investigation

Fig. 2. Dependence of strippant part upon pressure at 513 K

0.002 % even at 0.5 MPa at the possible temperature of the used air 313 K.

Taking into account above-mentioned, the pressure of approximately 3 MPa was sustained in all experiments. Such pressure ensured the liquid state of the main part of reactive medium within all investigated temperature range and minimum losses of raw material with the used air.

The losses during distillation of oxidate liquid phase were neglected at the calculations of material balances.

3. Results and Discussion

The results of temperature effect on the process proceeding are represented in Tables 3-5 and Fig. 3. The experiments were carried out without water.

As mentioned in Section 2, the soluble gums content and liquid phase acidity of oxidate and distillate (purified fuel) were determined for the analysis of oxidation degree of hydrocarbon raw material. The first value characterizes the amount of formed condensation and oxidation products which are inclined to further condensation and gumming

during operation or storage; the second value is the amount of acid soluble in the fuel components.

One can see from obtained results that the increase of temperature favors the increase of oxidation and condensation rates of sulphuric compounds as well as hydrocarbons. The yields of oxidate solid phase (products of final oxidation and condensation) and vat residue (concentrate of oxidized sulphuric compounds and liquid products of hydrocarbons oxidation) increase.

The soluble gums content, acidity of oxidate liquid phase and oxidate distillation products also increase at temperatures prior to 513 K. The decrease of acidity and soluble gums content at 553 K (compared with 513 K) is explained by the fact that condensation and oxidation processes proceed more deeply – the majority of oxidized and condensed structures is separated as the solid phase and vat residue, *pro tanto* less oxidation products remain.

The maximum sulphur removal degree for the purified fuel is achieved at 493 K. The following increase of temperature decreases the removal degree since the oxidation degree and accordingly, the sulphuric compounds removal, actually do not change at the

Serhiy Pysh'yev et al.

Table 3

Temperature effect on the products yield

No	Temperature, К	Yield, mas % calculated for raw material			
		Oxidate liquid phase	Oxidate solid phase	Distillate (refined fuel)	Vat residue
1	433	98.39	1.58	94.26	4.13
2	453	97.22	2.39	91.94	5.28
3	473	95.93	2.71	90.56	5.37
4	493	95.37	3.08	89.84	5.53
5	513	95.49	3.59	88.76	6.73
6	553	95.52	4.03	87.88	7.64

Table 4

Temperature effect on the quality of oxidate liquid phase

No	Temperature, К	Index		
		Content of total sulphur, mas %	Concentration of soluble gums, mg/100 cm^3	Acidity, mg KOH/100 sm^3
1	433	0.83	124	38.2
2	453	0.83	237	45.4
3	473	0.82	284	67.0
4	493	0.8	463	167.0
5	513	0.72	-	-
6	553	0.73	-	-

Table 5

Temperature effect on the quality of refined fuel

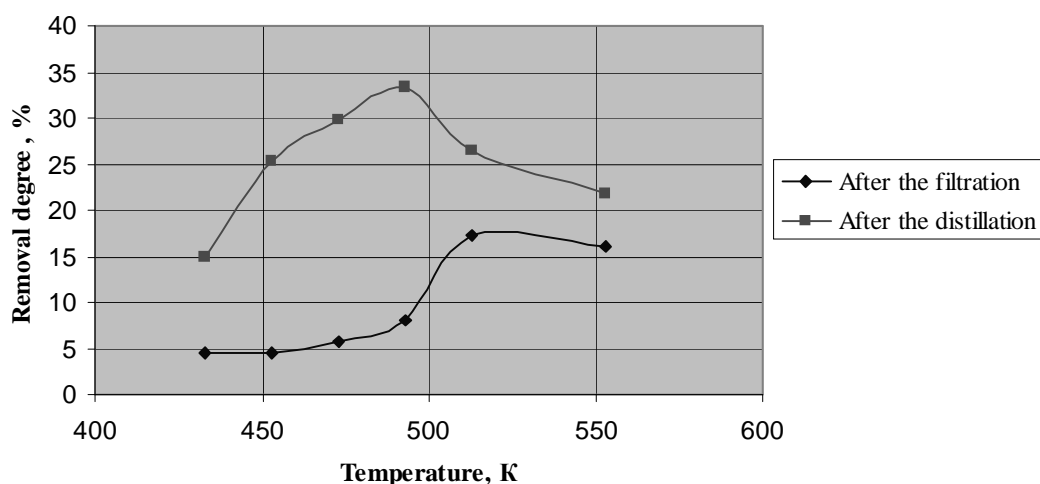| No	Temperature, К	Index		
		Content of total sulphur, mas %	Concentration of soluble gums, mg/100 cm^3	Acidity, mg KOH/100 sm^3,
1	433	0.74	25.6	4.2
2	453	0.65	41	10.5
3	473	0.61	42.3	23.7
4	493	0.58	47.5	44.2
5	513	0.64	64	77.3
6	553	0.68	33	52.1

Fig. 3. Dependence of sulphur removal degree upon process temperature

Table 6

Effect of water:raw material ratio on the products yield

No	Water:raw material ratio	Yield, mas % to calculated for raw material			
		Oxidate liquid phase	Oxidate solid phase	Distillate (refined fuel)	Vat residue
1	0:1	97.22	2.39	91.94	5.28
2	1:10	98.53	0.64	93.38	5.15
3	1:5	98.65	0.28	93.77	4.88
4	1:2.5	98.21	0.23	93.64	4.57
5	1:1	98.01	0.21	93.57	4.44
6	2:1	98.13	0.21	93.45	4.68
7	7:1	96.59	0.19	92.34	4.25
8	9:1	96.02	0.15	91.73	4.29

Table 7

Effect of water:raw material ratio on the quality of oxidate liquid phase

No	Water:raw material ratio	Index		
		Content of total sulphur, mas %	Concentration of soluble gums, mg/100 cm^3	Acidity, mg KOH/100 sm^3
1	0:1	0.83	237	45.4
2	1:10	0.80	86	44.0
3	1:5	0.78	82	41.5
4	1:2.5	0.77	63	40.1
5	1:1	0.81	41	33.55
6	2:1	0.82	35	22.6
7	7:1	0.85	18	11.3
8	9:1	0.84	19	11.2

Table 8

Effect of water:raw material ratio on the quality of refined fuel

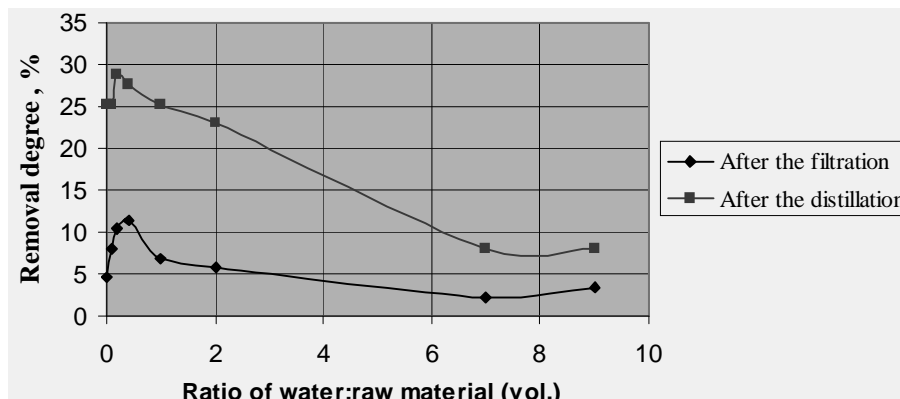| №	Water:raw material ratio	Index		
		Content of total sulphur, mas %	Concentration of soluble gums, mg/100 cm^3	Acidity, mg KOH/100 sm^3,
1	0:1	0.65	41	10.5
2	1:10	0.65	26	7.3
3	1:5	0.62	27	5.1
4	1:2.5	0.63	22	4.9
5	1:1	0.65	20	4.1
6	2:1	0.67	18	3.4
7	7:1	0.80	10	1.3
8	9:1	0.80	10	1.2

Fig. 4. Dependence of sulphur removal degree upon water:raw material ratio

temperatures of above 493 K, *i.e.* mass amount of such compounds in the purified product is constant.

Thus temperatures 453–493 K are the optimum temperatures.

The results concerning the effect of water are represented in Tables 6-8 and Fig. 4.

One can see that introduction of water into reaction medium inhibits the oxidation of hydrocarbon medium: soluble gums content, acidity of obtained products and yields of oxidation products (oxidate solid phase and vat residue) decrease. On the other hand, small portions of water practically do not influence the sulphuric compounds oxidation rate. Due to the increase of fuel yield the sulphur removal degree increases even at the water:raw material ratio 1:5 and 1:2.5.

At water:raw material high ratio (7:1 and 9:1) the fuel and oxidate yields decrease owing to the losses of raw material with water vapors and solubility of oxidation products in aqueous phase.

Depending on the fact that the increase of water amount decreases reactor productivity and increases its sizes, the optimum water:raw material ratio is 1:10–1:5.

4. Conclusions

It has been established that 453–493 K is the optimum temperature range for the oxidative desulphurization of 553–623 K fraction with the sulphur content of 0.87 mas %. The introduction of small amount of water (water:raw material ratio is 1:10–1:5) positively affects the process selectivity, essentially decreases the oxidation of hydrocarbon medium and does not change the sulphuric compounds oxidation rate.

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ВПЛИВ ТЕМПЕРАТУРИ ТА ВОДИ НА ПРОЦЕС ОКСИДАЦІЙНОГО ЗНЕСІРЧУВАННЯ ПРЯМОГОННОЇ ДИЗЕЛЬНОЇ ФРАКЦІЇ З ВИСОКИМ ВМІСТОМ СІРКИ

Анотація. *Вивчено вплив температури та співвідношення вода:сировина на процес оксидаційного знесірчування прямогонної дизельної фракції 553–623 К. Встановлено оптимальні значення температури та співвідношення вода:дизельна фракція для сировини, що містить 0,87 % мас. сірчистих сполук.*

Ключові слова*: десульфуризація, дизельне пальне, оксидацій не знесірчування, сірка, сульфоксиди, сульфони.*