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THEMATIC FIELDS

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SOCIETY & „INDUSTRY 4.0"

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SCIENTIFIC-TECHNICAL UNION OF MECHANICAL ENGINEERING "INDUSTRY 4.0"

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TECHNOLOGICAL BASIS OF "INDUSTRY 4.0". DOMINANT TECHNOLOGIES IN "INDUSTRY 4.0"

BUSINESS & "INDUSTRY 4.0". SOCIETY & „INDUSTRY 4.0"

SEDIMENT RECYCLE AFTER BIODIESEL PRODUCTION

ПЕРЕРАБОТКА ОСАДКОВ, ОБРАЗУЮЩИХСЯ ПОСЛЕ ПОЛУЧЕНИЯ БИОДИЗЕЛЯ

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The EU's energy policy is to increase the energy of renewable sources to 15% by 2020 with the production of biodiesel being ~ 7% of the total energy produced. In the field of transport energy supply the EU policy is to support the reduction of polluting gases emissions.

In 2014 biodiesel production amounted to 3.0 billion liters worldwide, ~ 90% of which was produced in Europe. The production and use of biodiesel in Germany has increased significantly due to tax exemption. This was facilitated by the established wide network of filling stations (1500).

It should be taken into account that biofuel is 1.5 times cheaper than gasoline and when biofuel is burned, just as much carbon dioxide (CO_2) is released into the atmosphere as absorbed by its plants which are its raw materials.

Table 1 shows the total amount of energy consumed when using various types of fuel.

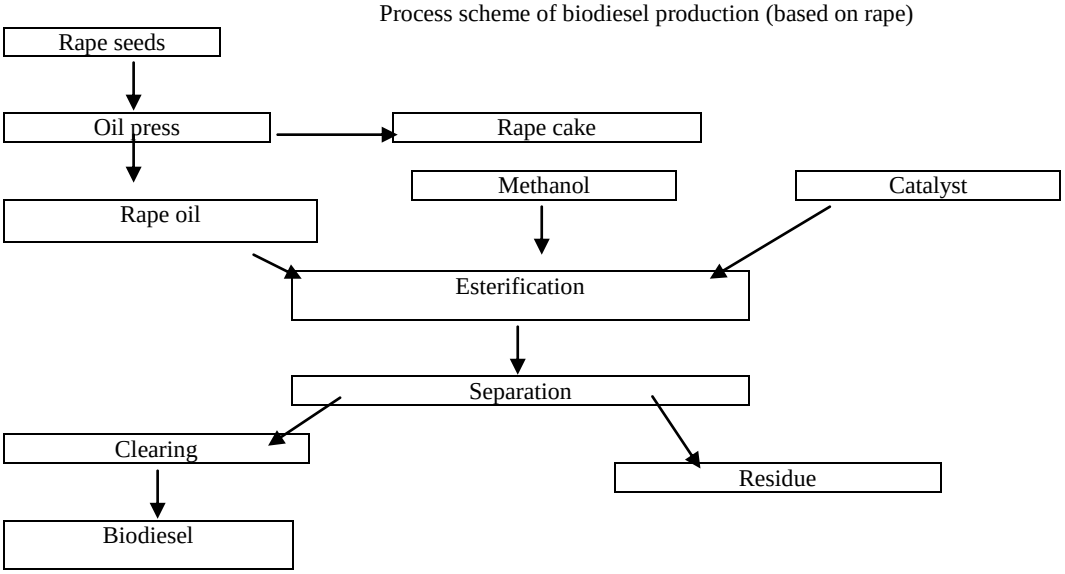
Table 1

Total amount of energy consumed when using various types of fuel (million tons).

Fuel	1990	2000	2010	2020	2030
Gasoline	132,0	130,0	142,0	145,0	141,0
Kerosene	29,0	45,0	53,0	63,0	72,0
Diesel	103,0	148,0	182,0	208,0	224,0

However, waste remained after biodiesel production pollutes the environment [1]. The process of production is represented in the scheme.

Process scheme of biodiesel production (based on rape)



The purpose of this research is to develop a technology for processing residues remained after biodiesel production in order to reduce environmental pollution.

The material of the research is the sediment remained at factories after biofuel production.

The object was initially examined chromatographically in order to establish the composition of sediment formed after biofuel production [2]. Sediment electro-oxidation was carried out in a conventional glass cell with a separated cathode and anode space in a 7M solution of potassium hydroxide (KOH) at various electrodes (Pt, Ni-Re, Ni_2B, Co_2B, Fe_2B) at different temperatures and sediment concentrations at the Sistem-500 potentiostat. The potential was measured relative to the mercury oxide reference electrode [3]. The degree of oxidation was judged not only by the polarization curves obtained, but also by the position and magnitude of the peaks in the IR spectra taken before and after the sediment oxidation. The substances obtained again after electrooxidation were identified using various physicochemical methods of UV, IR spectroscopy [4-6]. The sediment composition studied with a chromatograph is shown in Table 2.

Table 2

The composition of the researched sediment obtained during biodiesel production at various factories

N/N	Substance	Sediment fraction	Sediment fraction	Sediment fraction
1	Glycerin	83,60	97,80	95,00
2	Esters of methyl acids C-16:0	0,10	0,15	0,10
3	Esters of methyl acids C-16:0	0,40	-	-
4	Acids C-16:0	0,10	0,10	0,08
5	Acids C-18:N	-	0,40	0,35
6	Ester of methyl acid C-22:0	-	0,06	-
7	Monoglyceride	4,50	0,20	2,00
8	Ester of methyl acid C-18:0	4,50	-	2,50
9	∑ Esters of methyl acid C-18:1+2+3	2,20	2,00	0,20
10	∑ Esters of methyl acid C-18:N	0,60	-	-

As can be seen at the table above, the composition of sediment obtained at various factories differs insignificantly.

The polarization curves obtained at sediment electro-oxidation when producing biodiesel are presented in Fig. 1.

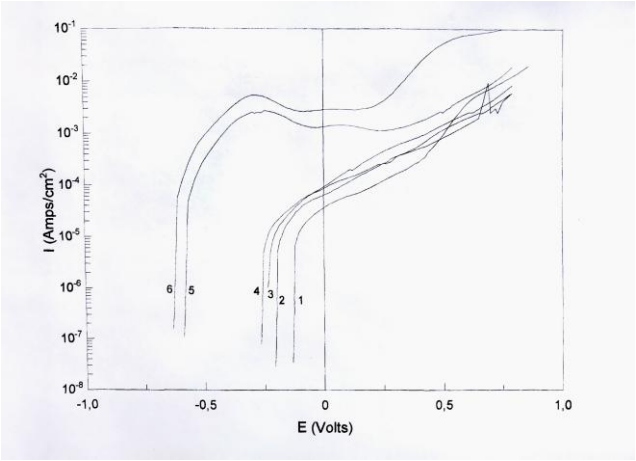


Рис 1. The polarization curves obtained at sediment electro-oxidation after biodiesel production: 1- smooth Ni; 2- Fe_2B; 3- Co_2B; 4- Ni_2B; 5- Ni-Re (303K); 6- Ni-Re (323K)

As can be seen at the figure, sediment electro-oxidation obtained in biofuel production increases for all the researched catalysts electrodes (Pt, Ni-Re, Ni_2B, Co_2B, Fe_2B) with increasing temperature and concentration in the alkaline solution (7M KOH), which is not unexpected . The potential of the working electrode was established in 3-5 minutes and was reproduced quite well while shifting into the field of large potentials with the researched sediment concentration increase. The maximum current density achieved on smooth platinum is ~ 10 mA / cm^2 at the potential of 0.3 V.

The researched catalysts (Pt, Ni-Re, Ni_2B, Co_2B, Fe_2B) were studied by X-ray diffraction analysis on unfiltered $Fe_{k\alpha}$ radiation (λ_{Fe} = 1,93 Angstrom). The URS-60 apparatus (the "powder" method, the Debye camera) was used for the X-ray check.

The Raney alloy was obtained by adding powdered nickel to the aluminum melt followed by cooling in air to room temperature. The alloy was then crushed to a powdery condition. The alloy leaching was carried out during a day in a 20% sodium hydroxide solution (NaOH). The content was then transferred to a stainless steel container and placed on a water bath for 8 hours. After the mentioned time the mother liquor was drained, the alloy was poured with a fresh 30% solution, placed in an autoclave, heated to a temperature of 353-363 K. The autoclave was cooled to a room temperature, the resulting alloy was washed with a 10% NaOH solution 3-5 times and then with distilled water to pH = 7. The resulting catalyst was stored in ethyl alcohol solution [7].

Borides of variable valence metals (Ni_2B, Co_2B, Fe_2B) were electrochemically obtained by using an electrolyte of the following composition: $NiCl_2 \cdot 6 \cdot H_2O$ (AR) - 120 g/l; $NaBH_4$ - 5g/l; NaOH - 40 g/l; Rochelle salt - 50 g/l; The bath temperature is 333 K; sedimentation time - 20 min. To slow down the hydrolysis reaction a strong alkaline medium pH>12 was used. $6Ni^{2+} + 5\ BH_4^- + 6H_2O + 7e \rightarrow 3\ Ni_2B + 2B(OH)_3 + 13\ H_2$

To establish the phase composition of the obtained borides not only X-ray phase analysis was used but the amount of boron was also determined. For that purpose the films were dissolved in "royal vodka" and boron was determined by the method [8].

Calculation of interplanar distances was carried out according to the Wolf-Brag formula [9]

$2d \sin\Theta = n\lambda$

The catalyst dispersion was carried out according to the Selyakov-Scherrer formula [10].

The crystal lattices parameters were calculated from quadratic forms for various syngonies (cubic, tetragonal, hexagonal) [11]. The results of the calculations are presented in Table 3.

Table 3

Parameters of crystal lattice in the Ni-Re alloy

Phase	Parameters of pure phases crystal lattice in the equilibrium condition			Parameters of the crystal lattice in the Ni-Re alloy		
	a , A^0	b, A^0	c,A^0	a , A^0	b, A^0	c,A^0
$Ni\ Al_3$	6,611	4,812	7,366	6,650	4,770	7,390
Ni_2Al_3	4,028	4,89	-	4,045	4,855	-
Ni Al	2,887	-	-	2,872	-	-
Ni_2B	-	-	-	4,985	-	4,253
Co_2B	-	-	-	5,027	-	4,222
Fe_2B	-	-	-	5,110	-	4,250

It is known that the catalytic activity of variable valency metal alloys depends not only on the nature and size of the catalyst surface but also on the d-characteristic surface [12].

There is a relationship between the d-characteristic, the number of electrons (z) above the argon shell and the radius of the single bond (R).

$R = 1{,}825\text{-}0{,}043z\text{-}(1{,}6\text{-}0{,}1z)\ \delta\ 10^{-2}$

There is another formula that expresses the relationship between single bond radius and fractional bond index (the ratio of valency to the coordination number)

$R = R_n + 0,3 \lg n$

So for δ we get:

$\delta = (1,825 - R_n - 0,3 \lg n - 0,043z) : (1,6 - 0,1 z)$;

The change in the crystal lattice parameter due to impurities introduction and the carrier nature will lead to a change in the catalytic activity, which we observe as a more complete sediment oxidation formed in the biofuel production on Ni-Re rather than on borides of variable valency metals.

To confirm the possibility of sediment electro-oxidation, production and identification of electro-oxidation products formed after biofuel production in alkaline electrolyte, an "Specord" IR spectrometer was used. Typical IR spectra of sediment oxidized on Ni-Re are shown in Fig. 2a, b

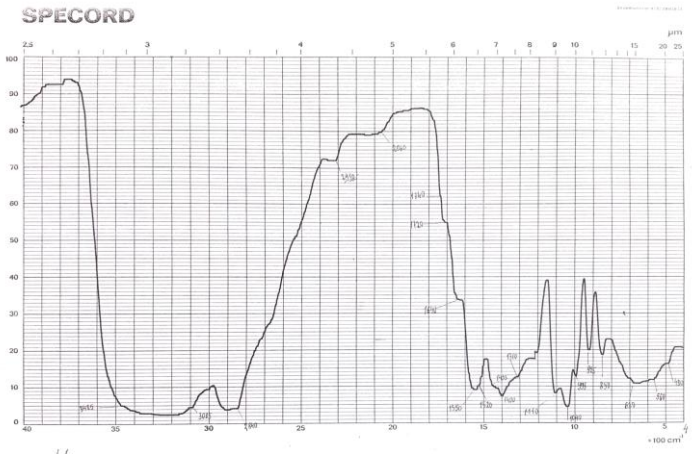


Fig. 2a

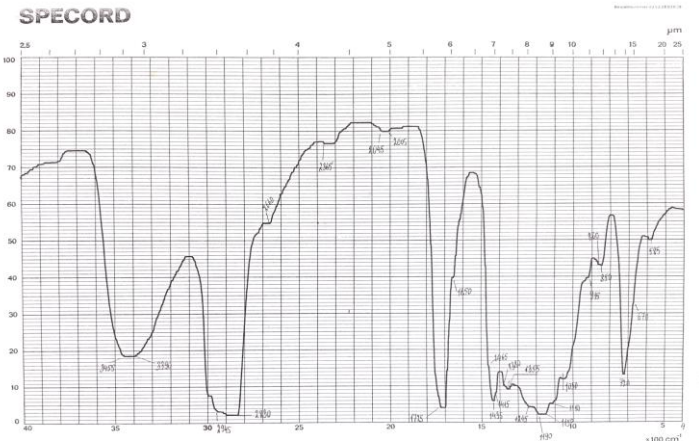
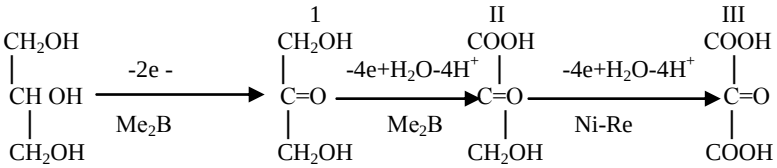


Fig. 2b

Fig. 2a,b. IR spectra recorded on the Specord spectrometer before (a) and after (b) sediment oxidation

As can be seen at the obtained spectra electro-oxidation shows significant changes in the wave number range of 2800-1550 cm^{-1} and 1550 - 650 cm^{-1}.

Sediment electro-oxidation can be represented by the following scheme



The obtained reaction products can be identified as: I-1,3-dihydroxypropanol (dihydroxyacetone), II-2-oxo, 3-hydroxypropanoic acid (hydroxyhydric acid), III-2-oxo-propanedioic acid (mesoxalic acid) - a component of lotions, emulsifiers, creams to intensify tanning, catalyst for the synthesis of esters.

This reaction was studied [13], nickel (I and II) and palladium applied to coal (III) were used as a catalyst. The use of other catalysts, Raney nickel (Ni-Re) and Me_2B borides allowed to increase the yield of the reaction product.

This research resulted in developing a technique for recycling waste generated in the biodiesel production.

It shows the possibility of a more complete electro-oxidation of generated waste using Ni - Re catalysts and a transition metal boride (Me_2B)

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