

Preparation and properties of hydrogen peroxide oxidized starch for industrial use

Nataša Karić¹, Jelena Rusmirović², Maja Đolić³, Tihomir Kovačević², Ljiljana Pecić⁴, Željko Radovanović¹ and Aleksandar Marinković³

¹Innovation Centre of the Faculty of Technology and Metallurgy Belgrade, Karnegijeva 4, 11070 Belgrade, Serbia

²Military Technical Institute, Ministry of Defense, Ratka Resanovića 1, 11000 Belgrade, Serbia

³University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11070 Belgrade, Serbia

⁴Technical College of Applied Studies in Mechanical Engineering Trstenik, Radoja Krstića 19, 37240 Trstenik, Serbia

1. EXPERIMENTAL

1. 1. Materials

Native wheat starch was purchased from Žito Promet Ruma Ltd. (moisture content ≤ 15.0 %, ash content on d.m. 0.46-0.55 %), while the chemical used for its modification: absolute ethanol and formic acid (≥ 99.8 and ≥ 98.0 %, respectively; ZORKA Pharma), potassium and sodium hydroxide (≥ 90.0 and ≥ 97.0 %, respectively; HeMoss, Belgrade), concentrated HCl (Lachema, Czech Republic), diethyl ether (≥ 99.0 %; Fisher UK), 30 % solution of hydrogen peroxide (Centrohém, Stara Pazova), iron(II) sulfate heptahydrate (≥ 98.0 %; Zorka, Šabac), copper(II) sulfate pentahydrate (99.9 %; Merck KgaA, Germany), copper(II) acetate monohydrate (99.0 %; Kemika, Zagreb), copper(II) chloride (98.0 %; Riedel-de Haën, Germany), citric acid (≥ 99.5 %; Sigma-Aldrich, Germany), hydroquinone (≥ 99.0 %; Fluka, Germany), tartaric acid and isopropyl alcohol (≥ 99.5 and ≥ 98.0 %, respectively; Merck KgaA, Germany).

1. 2. Methods

1. 2. 1. Laboratory isolation of ricinoleic acid

The isolation of ricinoleic acid from castor oil was performed analogously to previous published method [1]: 233 g (0.26 mol) of castor oil and 700 mL of absolute ethanol were placed into a four-neck-reactor equipped with reflux condenser, mechanical stirrer, thermometer, dropping funnel and nitrogen inlet. After dissolving of castor oil, the 30 % potassium hydroxide (0.91 mol) was slowly introduced in reactor with constant stirring. The reaction mixture was maintained at approximately 10 °C during the addition of potassium hydroxide for 1 h. Hereafter, the reaction mixture was heated to 50 °C and temperature was kept constant for 2 h. After that, two-thirds of the solvent was removed from the mixture by distillation at atmospheric pressure. The obtained slurry was dissolved in distilled water, acidified with concentrated HCl to pH 3.0, purified with activated carbon and filtered. The obtained ricinoleic acid (RA) was extracted by diethyl ether and the obtained solution was dried with anhydrous sodium sulfate, and then in vacuum dryer at 80 °C/2000 Pa for 5 h. The FTIR spectrum was presented in the section 3.1. Elemental analysis calculated for $C_{18}H_{34}O_3$ ($M_w = 298.46$ gmol⁻¹): C, 71.42; H, 10.32; O, 18.26. Found: C, 70.98; H, 10.31; O, 18.71. The oxygen percent was calculated as the difference to 100 %. NMR analysis (Fig. D1): ¹H-NMR (200 MHz, CDCl₃-d₆, δ / ppm): 0.88 (3H, s, C₁₈H₃), 1.31-1.35 (16H, m, $J = 11.0$ Hz, C₄₋₇, C₁₄₋₁₇H), 1.44 (2H, m, $J = 11.0$ Hz, C₁₃H), 1.62 (2H, m, $J = 7.0$ Hz, C₃H), 2.03 (2H, m, $J = 7.0$ Hz, C₈H), 2.22 (2H, m, $J = 7.0$, C₁₁H), 2.33 (2H, dd, C₂H), 3.63 (1H, m, C₁₂H), 5.39-5.53 (2H, m, C₉H and C₁₀H), 6.5 (1H, s, C₁₂OH), 9.65 (1H, s, C₁OH); ¹³C-NMR (50 MHz, DMSO-d₆, δ / ppm): 14.0 (C₁₈), 22.6 (C₁₇), 25.5 (C₁₄ and C₃), 28.9-29.3 (C₄₋₇ and C₁₅), 32.0 (C₁₆), 35.0 (C₂), 37.0 (C₁₁ and C₁₃), 71.7 (C₁₂), 125 (C₁₀), 133 (C₉), 179 (C₁).

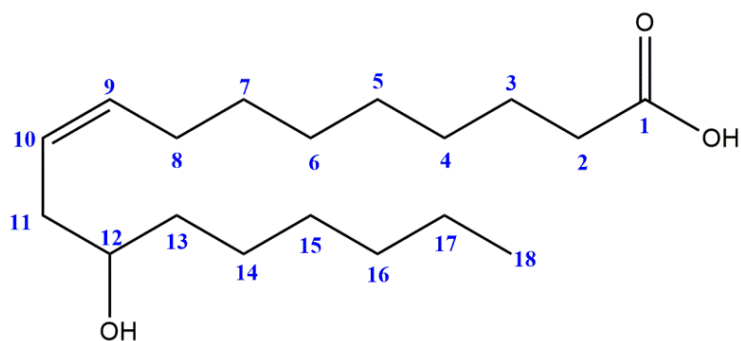


Figure D1. NMR analysis of ricinoleic acid

1. 2. 2. Laboratory epoxidation of soybean, linseed and sunflower oil

Firstly, 100 g of the soybean, linseed or sunflower oil (SO, LO and SFO, respectively) and 13.9 g of formic acid were poured to glass reactor immersed into water bath and mechanically stirred at the 50 °C and 550 rpm. Afterwards, 116.9 g of 30% hydrogen peroxide was gradually charged into the mixture during the 5 h. The molar ratio of soybean oil : formic acid : hydrogen peroxide was 1:2.64:8.9, which mean the molar ratio of carbon double bonds toward hydrogen peroxide ($C=C:H_2O_2$) were 1:1.7. After the charging of H_2O_2 was completed, the reaction further continued for the next 5 h. Hereafter, the mixture was cooled down, diluted with distilled water and subjected to extraction by diethyl ether to separate the oil product from the water phase. The final products, ESO, ELO and ESFO, were obtained after ether evaporation and drying at 40 °C/2000 Pa for 4 h. Epoxy number was determined using 0.4 M HCl in dioxane and titration with solution of silver nitrate in presence of the ammonium thiocyanate as indicator according to the standard method [2]. The obtained yield of epoxide is 68.9 %. The FTIR spectrum of ESO was presented in the section 3.1.

1. 2. 3. Laboratory synthesis of diisopropyl tartarate

In a single-neck flask, 25 g of tartaric acid was dissolved in 120 ml of isopropyl alcohol. Afterwards, the solution was cooled to 0 °C in an ice bath. The esterification of tartaric acid was catalyzed by introduction gaseous HCl for 5 h at 0 °C providing mixing at room temperature for 24 h. The excess ethanol was removed by distillation at 40 °C, and diisopropyl tartarate (DIPT), purified by vacuum distillation, as a mildly viscous yellow liquid (b.p. 85 °C/2500 Pa; refractive index 1.437). The FTIR spectrum was presented in the section 3.1. Elemental analysis calculated for $C_{10}H_{18}O_6$ ($M_w = 234.25 \text{ g mol}^{-1}$): C, 51.27; H, 7.75; O, 40.98. Found: C, 51.25; H, 7.70; O, 40.91. The oxygen percent was calculated as the difference to 100 %. NMR analysis (Fig. D2): $^1\text{H-NMR}$ (200 MHz, $\text{CDCl}_3\text{-d}_6$, δ / ppm): 1.35 (12H, dd, $6C_{1-3}\text{H}$ and $6C_{9-10}\text{H}$), 3.10 (2H, s, $C_5\text{OH}$ and $C_6\text{OH}$), 4.60-4.90 (4H, m, $4C_{2,5,6,8}\text{H}$); $^{13}\text{C-NMR}$ (50 MHz, DMSO-d_6 , δ /ppm): 22.0 (C_1 , C_3 , C_9 and C_{10}), 70.0 (C_2 and C_8), 73.0 (C_5 and C_6), 171 (C_4 and C_7).

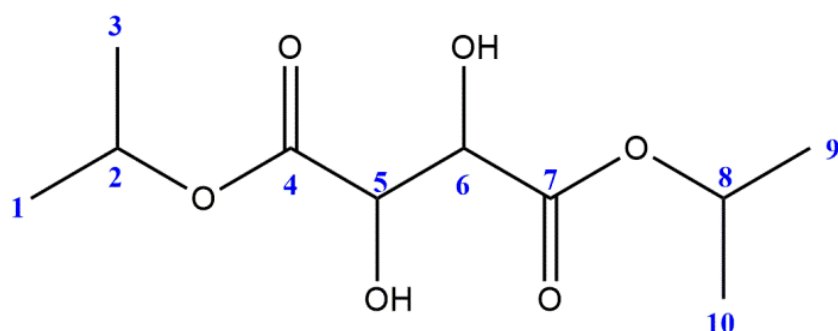


Figure D2. NMR analysis of diisopropyl tartarate

1. 2. 4. Laboratory synthesis of copper citrate

In a typical experiment, 4.2 g of citric acid dihydrate (0.02 mol) and 3.41 g copper chloride dihydrate (0.02 mol) were dissolved in 100 ml of distilled water. The resulting light blue solution was filtered and heated in an oven at 85 °C for

19 h in a Teflon reactor. The green crystalline product was separated from the blue solution (pH 4.0) by decantation, thoroughly washed with distilled water, and air-dried (yield 3.2 g, 90 % based on Cu). Cu content, determined according to atomic absorption spectroscopy, was 24.5 %. The FTIR spectrum was presented in the section 3.1.

1. 2. 5. Laboratory synthesis of copper ricinoleate

The copper(II) acetate monohydrate in amount of 6 g (0.03 mol) was poured to flask and dissolve in ethanol with stirring at room temperature. Afterwards, 60 ml (0.210 mol) of ricinoleic acid (*synthesis 1. 2. 1*) is slowly added during 2 h while the reaction mixture was heated to 80 °C. pH (6.5-7.0) was adjusted with sodium hydroxide. After that, the obtained mixture was cooled down and dried in vacuum dryer to evaporate the solvent. Cu content, determined according to atomic absorption spectroscopy, was 7.4 % (78 % conversion; the product contain ~20 % of non-reacted ricinoleic acid and its content was adjusted by experimental condition to provide plasticizing effect in the course of starch oxidation). The FTIR spectrum was presented in the section 3.1.

1. 2. 6. Laboratory preparation of oxidized starch by the SPS method

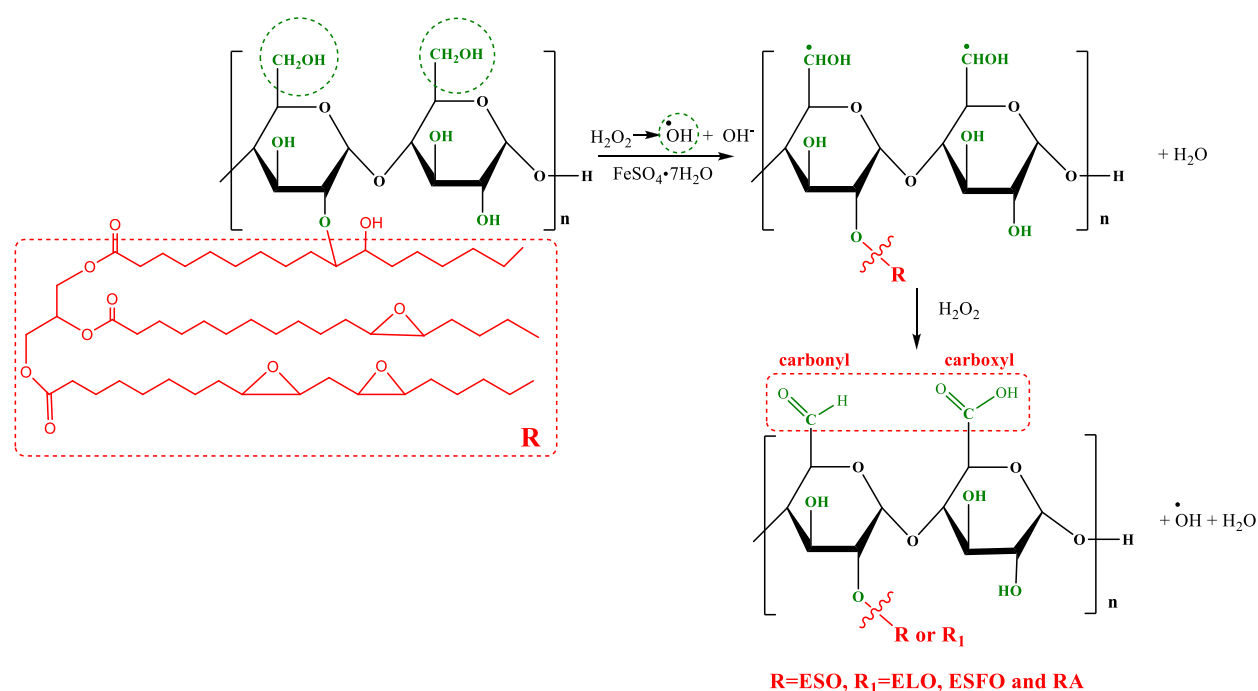


Figure D3. Proposed mechanism of starch oxidation with hydrogen peroxide [3-4]

1. 3. Industrial starch oxidation by the SPS method

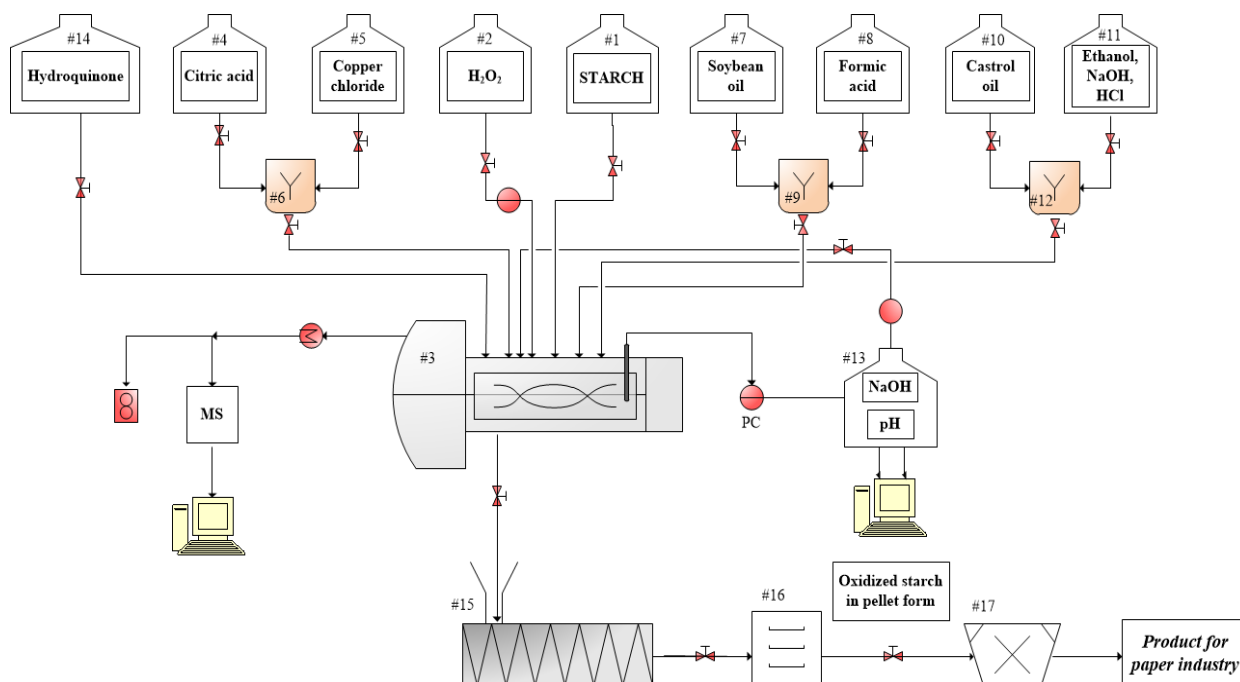


Figure D4. Schematic overview of the technological process for the starch oxidation

2. CHARACTERIZATION

The carboxyl/carbonyl content and the swelling capacity (SC)/water solubility (WS) of native and oxidized/modified starch were determined as described in the previous publications [5-6], respectively. Carboxyl group content (%) was calculated as follows [7]:

$$\frac{\text{Milliequivalents of acidity}}{100 \text{ g starch}} = \frac{\text{sample} - \text{blank volume, mL} \times \text{Normality of NaOH} \times 100}{\text{Sample weight (dry basis), g}}$$

$$\text{Carboxyl content, \%} = \frac{\text{milliequivalents of acidity}}{100 \text{ g starch}} \times 0.045$$

Carbonyl group content, %, was calculated as follows [7]:

$$\text{Carbonyl content, \%} = \frac{\text{blank} - \text{sample volume, mL} \times \text{acid normality} \times 0.028 \times 100}{\text{sample weight (dry basis), g}}$$

The three measurements were performed, and standard deviation was less than 3%.

The viscosity of oxidized starches obtained at laboratory level was determined using capillary viscometer (Cannon-Fenske viscometer) (CF Method) following the method (Method 1) described in the publication [8]. The viscosity of oxidized starches obtained at industrial level was measured using Brookfield rotational viscometer (Brookfield DV-II + Pro Viscometer) (B Method) according to already described procedure [9] with some changes: before measuring oxidized starch was heated at 90 °C for 30 min, and in the course of cooling from 60 °C viscosity was continuously recorded.

Fourier transforms infrared (FTIR) spectra of the samples were recorded in absorbance mode using a Nicolet™ iS™ 10 FT-IR Spectrometer (Thermo Fisher SCIENTIFIC) with Smart iTR™ Attenuated Total Reflectance (ATR) Sampling accessories, within a range of 400-4000 cm⁻¹, at a resolution of 4 cm⁻¹ and in 20 scan mode.

Nuclear magnetic resonance (¹H NMR and ¹³C NMR) spectra were recorded in a deuterated chloroform (CDCl₃) using a Ascend 400, Bruker, USA, at 400 MHz and 25 °C.

Thermogravimetric (TG) and differential scanning calorimetry analysis (DSC) (SDT Q600 simulated TGA-DTA instrument - TA Instruments) were used for studying the thermal properties of oxidized starches. Samples were heated to 800 °C (10 °C min⁻¹) in a flow of nitrogen (20 cm³ min⁻¹). The morphology of native and modified starches was recorded by a scanning electron microscope (SEM) (FE-SEM, TESCAN Mira3 XMU) operated at 20 kV. Before analysis, oxidized starch products were coated with Au.

3. RESULTS AND DISCUSSION

3. 1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of synthesized plasticizers RA, ESO and DIPT are shown in Figure D5. The absorption peak at 1710 cm⁻¹ at FTIR spectrum of RA belongs to the C=O stretching of carboxylic acid. Noticed vibration at 1241 cm⁻¹ belongs to C–O stretching originates from epoxides confirming the successful of epoxidation of soybean oil which is agree with the previous study [9]. The peak at 1740 cm⁻¹ at spectrum of DIPT originates from the C=O stretch vibration of the esters groups. The absorption peaks at 1404 and 1606 cm⁻¹ at FTIR spectra of Cu citrate [10] and Cu ricinoleate reflect the symmetric and asymmetric stretch from carboxylic acid salts, respectively.

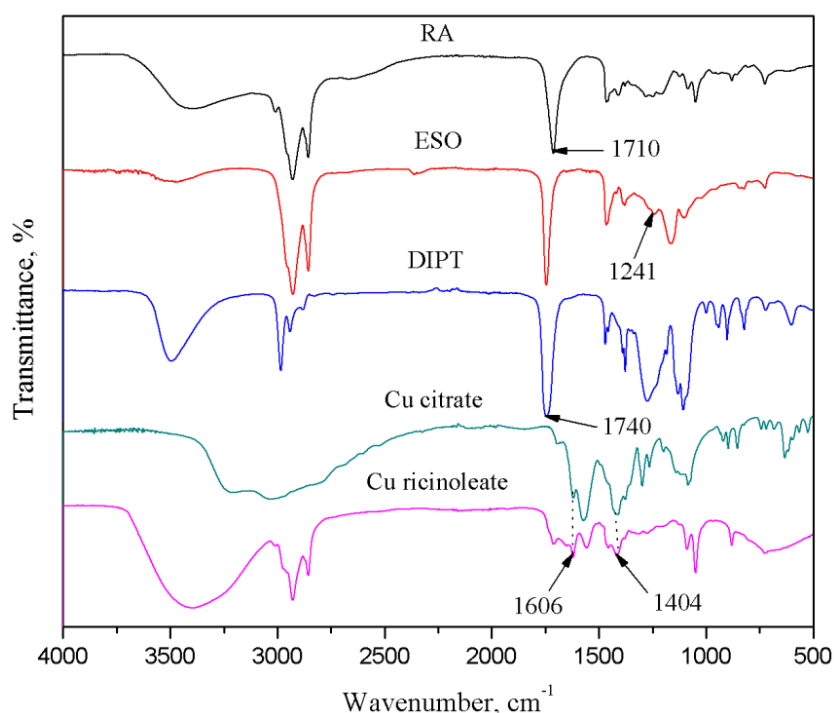


Figure D5. FTIR spectrum of RA, ESO, DIPT, Cu citrate and Cu ricinoleate

Table D1. Area of the characteristic groups in the region of carbonyl and carboxyl vibrations

Sample	Wavenumber, cm ⁻¹	Area, cm ²
Exp 1	1728	134.621
	1708	63.414
Exp 8	1726	136.356
	1710	58.203
	1748	219.932
Exp 10	1735	243.540
	1719	71.144
Exp 16	1744	40.562
	1732	184.328
	1710	166.902

3. 2. Carboxyl and carbonyl contents

Table D2. Carboxyl and carbonyl contents of native and oxidized starches obtained at the laboratory level

Sample	Carboxyl group content, %	Carbonyl group content, %	Sum, %*
Native starch	0.018	0.026	0.044
Exp 1	0.172	0.250	0.422
Exp 2	0.258	0.292	0.550
Exp 3	0.144	0.271	0.415
Exp 4	0.216	0.279	0.495
Exp 5	0.117	0.172	0.289
Exp 6	0.175	0.213	0.388
Exp 7	0.072	0.355	0.427
Exp 8	0.108	0.318	0.426
Exp 9	0.162	0.229	0.391
Exp 10	0.127	0.285	0.393
Exp 11	0.123	0.219	0.342
Exp 12	0.124	0.227	0.351
Exp 13	0.123	0.221	0.344
Exp 14	0.060	0.368	0.428
Exp 15	0.096	0.367	0.463
Exp 16	0.182	0.248	0.430
Exp 17	0.076	0.350	0.426

*Sum - the number of aldehyde and carboxyl groups per glucose units and can be ranging between 0 and 3

Table D3. Carboxyl and carbonyl contents of native and oxidized starches obtained at the industrial level

Sample	Carboxyl group content, %	Carbonyl group content, %	Sum, %*
Native starch	0.018	0.126	0.144
Exp 18	0.162	0.335	0.497
Exp 19	0.192	0.288	0.480
Exp 20	0.181	0.280	0.466

*Sum - the number of aldehyde and carboxyl groups per glucose units and can be ranging between 0 and 3

Table D4. D-optimal design with two factor and three replicates used to optimize the starch oxidation

Run	Factor 1 - T, °C	Factor 2 - H ₂ O ₂ volume, cm ³	Response - Carboxyl group content, %
1	50	2.5	0.188
2	80	3	0.238
3	80	1	0.088
4	20	2.5	0.113
5	80	3.6	0.258
6	45	2	0.174
7	50	2.3	0.192
8	20	1	0.062
9	35	1.6	0.144
10	65	4	0.235
11	20	4	0.144
12	40	1	0.074
13	20	4	0.144
14	65	1.8	0.204
15	65	4	0.235
16	50	1	0.0785
17	80	4	0.257
18	20	1	0.062

An increase in carboxyl group content is observed with increasing the temperature and initial concentration of H_2O_2 . According to the results given on Figure D6, as an operational parameters temperature of 80 °C (353 K) and 3.6 ml of H_2O_2 are selected as the most efficient for starch oxidation in presence of iron(II) sulphate catalyst. Similar results is obtained using copper(II) sulfate (differences not higher than 8 %; data not presented), which means that both catalyst showed similar activity which depends on metal ion activity and the water content (starch moisture and provided by water solution containing catalyst). Obtained results also indicate significance of the temperature as reaction parameter. Higher temperature (80 °C) means better hydrogen peroxide/water diffusivity and interior material availability (partial starch grain gelatinization occurs).

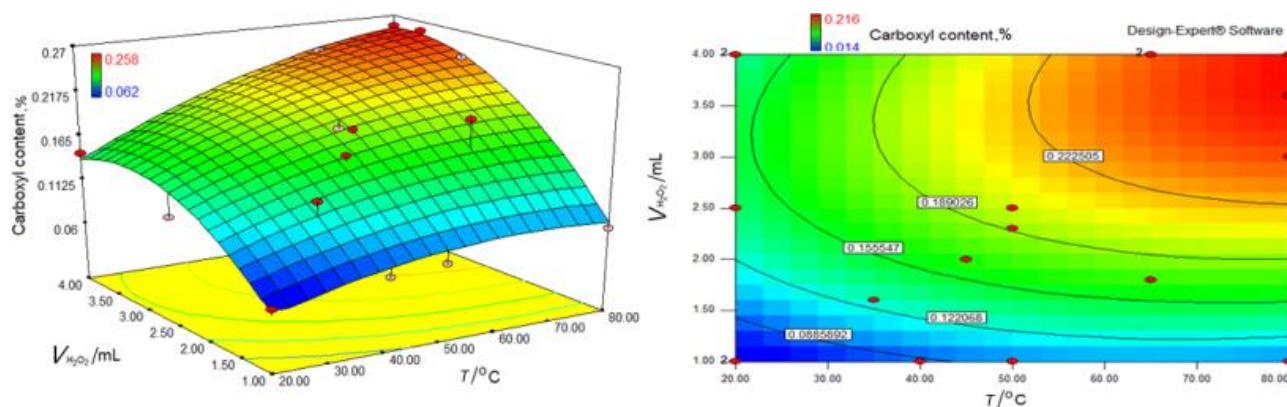


Figure D6. The influence of temperature (T , °C) and concentration of H_2O_2 (ml) on the value of carboxyl content (%) (a) 3D plot and (b) 2D plot

3. 3. Swelling capacity (SC), water solubility (WS) and viscosity (η)

Table D5. Swelling capacity (SC), water solubility (WS) and viscosity (η)* of native and oxidized starches obtained at the laboratory level

Sample	SC, %	WS, %	η / Pa s
Native starch	11.8	19.2	1.0630
Exp 1	22.7	38.6	0.0124
Exp 2	25.2	42.8	0.0121
Exp 3	19.7	33.5	0.0195
Exp 4	21.8	37.1	0.0183
Exp 5	18.3	31.2	0.0273
Exp 6	20.4	34.7	0.0252
Exp 7	16.3	27.8	0.0339
Exp 8	17.5	29.9	0.0313
Exp 9	23.9	36.2	0.0153
Exp 10	23.1	34.1	0.0175
Exp 11	22.7	32.8	0.0182
Exp 12	21.3	32.3	0.0189
Exp 13	21.5	31.5	0.0183
Exp 14	15.4	25.6	0.0323
Exp 15	18.6	29.3	0.0298
Exp 16	24.6	38.5	0.0141
Exp 17	16.5	28.2	0.0320

*determined by CF Method

Table D6. Swelling capacity (SC), water solubility (WS) and viscosity (η)** of native and oxidized starches obtained at the industrial level

Sample	SC, %	S, %	η / Pa s
Native starch	11.8	19.2	1.0630
Exp 18	16.1	29.8	0.0451
Exp 19	19.5	32.3	0.0440
Exp 20	18.3	31.9	0.0452

**determined by B Method

3. 4. Thermogravimetric analysis

Table D7. Thermal characteristics of native and oxidized starch

Sample	T_5 / °C	T_{50} / °C	Residue content, wt%	T_{DTG} / °C
Native starch	248.3	312.9	13.72	314.5
Exp 1	251.4	308.7	16.59	307.4
Exp 6	271.9	307.2	16.89	305.0
Exp 10	273.4	305.9	17.48	308.3
Exp 16	277.8	308.7	18.16	305.7

 T_5 and T_{50} are temperature at 5 and 50 mass % loss of the specimen, respectively.

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