

Optimization of (2E)-3,7-dimethyl-2,6-octadien-1-ol (geraniol) transformation process parameters using Response Surface Method (RSM)

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This paper presents the results of studies on the transformation of geraniol (GA) in the presence of the natural mineral bentonite. The paper determines the influence of temperature, catalyst content, and reaction time on the course of the process. In order to determine the most favorable process conditions, the catalytic tests were carried out without solvent and under atmospheric pressure. Three functions were chosen to determine the most favorable process conditions: GA conversion and the selectivities of the main products: linalool – LO and beta-pinene – BP. In addition, the paper optimize GA transformation process based on response surface methodology (RSM). The impact of the most relevant process indicators was presented. For all factors of the method, their effects on all primary parameters were determined in the form of second-degree polynomials, and such process conditions were determined to achieve their maximum.

Keywords: geraniol, bentonite, linalool, beta-pinene, optimization.

INTRODUCTION

Terpenes are an extremely interesting group of organic compounds with diverse flavors and aromas, as well as medicinal properties. Among them, monoterpenes stand out – volatile compounds found in the essential oils of many plants. Approximately more than 400 structures are known, the slight differences in their molecular structure determining their taste, aroma and medicinal properties. The high variability of the properties of monoterpene compounds allows their practical use in various fields of industry. Due to their anticancer, chemopreventive, antimicrobial, anti-inflammatory or immunomodulatory properties, they can find applications in modern oncology and other branches of medicine. Due to the fact that the most valuable terpenes are found in nature in small quantities, developing ways to produce them under laboratory conditions based on chemical methods is extremely important. A convenient method is the transformation of cheap and readily available substrates, such as geraniol. In the transformation of natural precursors, with the participation of catalysts of natural origin, valuable bioactive products such as linalool, beta-pinene, citral, nerol and farnesol can be obtained. These compounds, in addition to their olfactory properties, show activity in inhibiting the growth of many types of cancer, among other things¹.

Geraniol is a monoterpene alcohol with a pleasant rose scent. It is an important addition to numerous essential oils and is used commercially as a fragrance in cosmetic and household products. Geraniol is one of the main components of rose oil, giving it its characteristic scent. Rose oil is used in the cosmetic and perfume industry. Plants from the *Pelargonium* genus, often referred to as geraniums, contain geraniol in their leaves and flowers, imparting them with a distinctive, fresh aroma. Lemon oil is a natural source of geraniol, hence lemon fruits exhibit a delicate, citrusy scent. Lavender is known for its relaxing aroma, attributed to the presence of geraniol in its essential oil. This plant, also known as lemon

verbena, contains geraniol in its leaves, giving them a strong lemony fragrance. Palmarosa is a grass native to India, and its essential oil is rich in geraniol, lending it a rose-like fragrance¹⁻³.

Terpenes are a large and diverse class of organic compounds produced by various plants around the world. Because of their strong smell, they often protect the plants that produce them from herbivores. Geraniol is also produced by the scent glands of honey bees to mark flowers. It is also commonly used as an insect repellent, particularly for mosquitoes. Geraniol is mainly used to improve the fragrance of personal care products. In cosmetics, it can be found in lipsticks, skin and hair care products and aftershave preparations, among others. Essential oils that contain geraniol in their composition are mainly used in anti-aging and firming skin care products. Geraniol, in addition to its olfactory and flavorful properties, exhibits cytotoxic, anti-inflammatory, hepatoprotective, cardioprotective and neuroprotective effects. In addition, it has an antidepressant effect. An exceptionally interesting property of it is its mite-killing effect against house dust mites²⁻⁶.

Fajdek-Bieda et al. studied the GA transformation process using two natural zeolites: sepiolite⁷ and clinoptilolite⁸. The study evaluated the influence of such parameters as temperature (in the range of 80 to 150 °C), catalyst content (in the range of 5 to 15 wt%), and reaction time (in the range of 15 to 1440 minutes). The process carried out in the presence of sepiolite resulted in such products as: β -pinene (BP), ocimene (OC), linalool (LO), nerol (NE), citral (CL), isocembrol (IC) and thumbergol (TH). The highest selectivity (19 mol%) was obtained for LO. When clinoptilolite was used, the main products included 6,11-dimethyl-2,6,10-dodecatrien-1-ol (DC) and thumbergol (TH). The highest selectivity values of DC (14 mol%) and TH (47 mol%) were obtained at 140°C for the catalyst content of 12.5 wt% and for the reaction time of 180 min.

The article by Fajdek-Bieda et al.⁹ presents research related to the transformation of geraniol (GA), leading to

products with very valuable properties. In the proposed method, heterogeneous catalysts of natural origin in the form of alum and diatomite were used as catalysts. In the course of catalytic studies, the influence of such important parameters on GA transformations was determined: temperature from 80 to 150 °C, catalyst content from 5 to 15 wt% and reaction time from 15 min to 24 h. The tests presented in the article were carried out under atmospheric pressure (in air), as well as without any solvent. The optimal conditions for the transformation of GA were determined by its conversion and the selectivity of its transformation to the main products: beta-pinene (BP), 6,11-dimethyl-2,6,10-dodecatrieno-1-ol (DC) and thumbergol (TH). The above products were formed with the highest selectivity, respectively: 100 mol%, 50 mol% and 52 mol%. The synthesis results showed that for GA, the best transformation results were obtained at 80 °C (for both catalysts tested), at the catalyst content of 1 wt% (for both catalysts tested) and for the reaction times of 1 h (for diatomite) and 3 h (for alum).

The next work Fajdek-Bieda et al.¹⁰ presents the results of studies on the GA transformation process in the presence of the natural minerals montmorillonite (MMT), mironekuton (MIR), halloysite (HAL), as well as in the presence of halloysite modified with 0.1 M aqueous H₂SO₄ solution (HAL-MOD). The studies show that conducting syntheses at higher temperatures, with higher catalyst content and using long reaction time, resulted in the formation of polymerization products or products undesirable in the process, which negatively affected the overall analytical performance of the process. The comparison the results for the studied catalysts showed that for the catalyst HAL-MOD, despite the small BET surface area, obtained the most favorable conditions for the GA transformation process (low temperature, catalyst content and short time). Equally favorable conditions were obtained for MMT, which may be due to its strongly developed BET surface area and relatively large V_{por}. MIR was characterized by the very small BET surface area, while a large V_{por} and V_{microp}. which definitely influenced the results obtained. In summary, based on the obtained results, it was concluded that each of the studied parameters significantly influenced the course of geraniol transformations. Both the structure and morphology of the minerals used had a significant impact on the resulting products. The washing of HAL with sulfuric acid undoubtedly influenced the obtained results. Due to the undeveloped specific surface area, it can be assumed that the reaction in the presence of HAL-MOD as the catalyst took place on its surface.

Bentonite is a calcareous sedimentary rock. It is characterized by a very good absorption capacity. Therefore, it is widely used in various fields. These include the cosmetic, pharmaceutical, food industries and agriculture. Bentonite is also used as a soil improver or as a cat litter. It is also characterized by detoxifying and antimicrobial properties. It has a soothing effect on irritated skin, such as acne, and promotes wound healing. Bentonite clay in the form of poultices relieves pain and helps to reduce swelling after insect bites. Bentonite is usually found in gray, white, greenish and even yellowish colors. Its main ingredient is montmorillonite, which belongs to the silicate group. Its composition includes many minerals.

These include magnesium, calcium, silicon, potassium, iron, aluminum, manganese, sodium, zinc and copper^{11,12}.

Bentonite consists of small plates (or flakes) of silicon and aluminum oxide, along with sodium (Na) and calcium (Ca) cations. These plates have many ordered sheets arranged in a crystal lattice. When bentonite is dry, its lattice structure is closed. However, when the bentonite is dispersed in water, it causes the sheets to separate, eventually forming the large open lattice structure with the huge surface area. When the lattice structure opens, it exposes exchangeable sodium or calcium ions, which gives the bentonite an overall negative charge. Bentonite is always electrically unbalanced by atoms that have displaced aluminum - elements such as magnesium, iron and calcium. The result is a positively charged space between the layers. This space is filled with cations (negatively charged molecules), which are located, but poorly held, near the tetrahedral layers and which help balance the charge. Cations are remarkably mobile and can be replaced or exchanged for almost any other cation. This ability to exchange cations is an important feature of bentonite (Fig. 1)¹³.

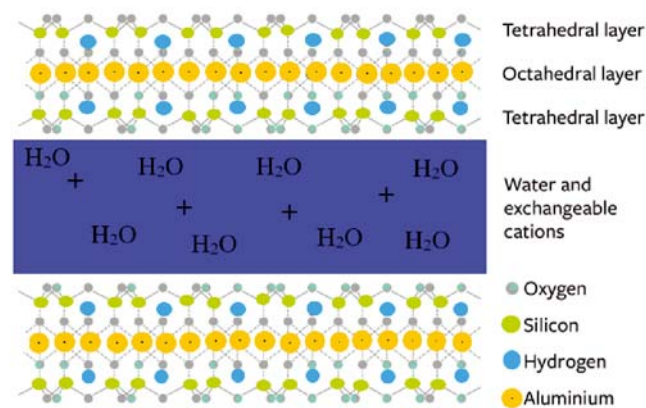


Figure 1. Structure of bentonite

Most industrial applications of bentonite involve using its swelling properties to form viscous aqueous suspensions. Depending on the proportion of clay and water, such mixtures are used as binders, plasticizers and suspending agents¹⁴. The highly developed surface of bentonite makes it used to stabilize emulsions or as a medium for transferring other chemicals. In addition, bentonite chemically reacts with many chemicals to form compounds that are mainly used as gelling agents in various organic liquids^{15,16}.

Optimization means to enhancing the functioning of a structure, process or product in order to obtain full benefits. The term optimization is generally used in the analytical chemistry as a way of finding the circumstances under which to apply a procedure that gives the best possible answer¹⁷. In the analytical chemistry, when performing optimization, one parameter is usually studied. While only one constraint is different, others are kept steady. Therefore, this method does not correspond to the full impact of a parameter on the answer. Another disadvantage of single-factor optimization is that it increases the number of tests needed for a study, resulting in longer time and higher costs, as well as greater use of chemicals and raw materials^{17,18}.

The compositional master plan is one of the most popular forms of RSM, used to optimize various processes related to food and plants, such as the extraction process of bioactive compounds^{19–21}, milling²², plant fermentation processes²³ or production of dietary starch products²⁴. To date, the RSM method has been used in the following chemical processes: optimization of the extraction process of phenolic compounds with antiradical activity from white mulberry leaves²⁵, optimization of the process of simultaneous hydrolysis and fermentation of native starch²⁶, optimization of the parameters of the process of leaching zinc oxide with ammonia and ammonium bicarbonate solutions²⁷, optimization of bio-production of citric acid in deep culture of *Aspergillus niger* carried out in the presence of Tween 80²⁷.

The purpose of this work was to determine the most favorable conditions for the obtaining geraniol transformation products using bentonite as the catalyst. The first part of the work deals with preliminary studies determining the effects of temperature, catalyst content and reaction time on the course of GA transformation under atmospheric pressure. The presented technology has a number of advantages, such as the use of reduced reaction temperature, low catalyst content and sufficiently short reaction time. In addition, the syntheses are carried out without the presence of solvent, which excludes the likelihood of its reaction with GA and transformation products (Scheme 1). In addition, there is no need to recover and recycle the solvent.

In addition, so far the process of geraniol transformation in the presence of bentonite has not been optimized. The proposed RSM method allows the selection of optimal parameters, such as temperature (50–150°C), amount of catalyst (1–10 wt%) and reaction time (0.25–24 h), taking into account the high values of conversion of geraniol and the selectivity of appropriate products (beta-pinene and linalool).

MATERIALS AND METHOD

Raw Materials

The syntheses were carried out in the presence of bentonite (100% pure, Nanga, Hobbs, New Mexico) as

the catalyst. The organic raw material used in the study was GA (99% pure, from Acros Organics, Milwaukee, USA). For quantitative analysis, which was carried out by gas chromatography (GC), the following standards were used: citronellol (95% pure, from Sigma Aldrich, Steinheim, Germany), citral (95% pure, from Sigma Aldrich, Steinheim, Germany), ocymentene (90% pure, from Sigma Aldrich, Milwaukee, WI, USA), beta-pinene (95% pure, from Fluka, Milwaukee, WI, USA), linalool (97% pure, from Acros, Steinheim, Germany), farnesol (96% pure, from Acros, Steinheim, Germany), nerol (97% pure, from Acros, Steinheim, Germany), myrcene (technically pure, from Sigma Aldrich, Steinheim, Germany), and geranylgeraniol (85% pure, from Sigma Aldrich, Milwaukee, WI, USA).

Characterization of bentonite

The following analytical techniques were used to determine the structure of bentonite:

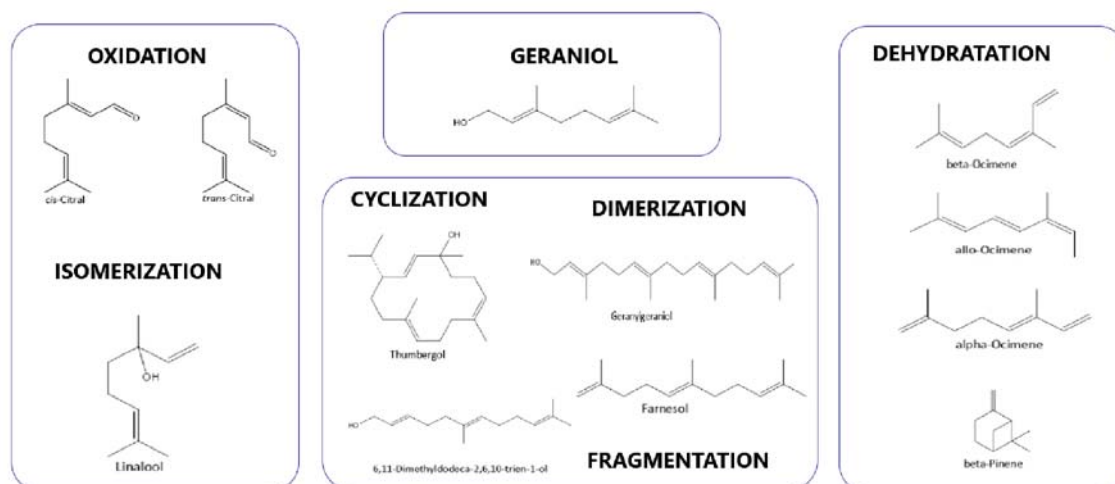
a) X-ray diffraction (XRD): An Empyrean X-ray diffractometer with a Cu K α radiation source (Malvern Panalytical, Grovewood, UK) was used. Samples were analyzed in the temperature range from 5 to 30 degrees with a step of 0.02 degrees,

b) Elemental mapping: Scanning electron microscopy (SEM) with an EDX detector from JEOL, model JSM-6010LA (Tokyo, Japan) was used. Elemental composition analysis was carried out using an Epsilon3 energy dispersive X-ray fluorescence spectrometer (EDXRF) from Malvern Panalytical (Grovewood, UK),

c) FT-IR spectroscopy: FT-IR spectroscopy studies were carried out using a Thermo Nicolet 380 instrument (Malente, Germany) in the wavelength range of 400 to 4000 cm⁻¹.

Method of Transformations of Geraniol and Analyses of the Post-Reaction Mixtures

The syntheses were carried out in a glass reactor with a capacity of 25 cm³, which was equipped with a reflux condenser and a magnetic stirrer with a heating function. The ranges of the studied parameters were as follows: temperature 80–150 °C, catalyst content 5–15 wt%, and reaction time from 15 min to 24 h (Fig. 2). In order to perform qualitative and quantitative analyses, the samples



Scheme 1. Diagram of the main chemical reactions taking place during the transformations of GA

of the post-reaction mixtures were first centrifuged and then they were dissolved in acetone in the ratio 1:3.

Qualitative analyses were performed using the GC-MS method on a ThermoQuest apparatus with a Voyager detector and a DB-5 column (filled with phenylmethylsiloxanes, 30 m × 0.25 mm × 0.5 mm). Analysis parameters: helium flow 1 mL/min, sample chamber temperature 200 °C, detector temperature 250 °C, oven temperature—isothermally for 2.5 min at 50 °C, then heating at the rate of 10 °C/min to 300 °C.

Quantitative analyses were performed with help of Thermo Electron FOCUS chromatograph with FID detector and TR-FAME column (cyanopropylphenyl packed, 30 m × 0.25 mm × 0.25 mm). The analysis parameters were as follows: helium flow 0.7 mL/min, sample chamber temperature 200 °C, detector temperature 250 °C, oven temperature—isothermally for 7 min at 60 °C, then heating at the rate of 15 °C/min to 240 °C.

The quantitative analyses of the products were performed using the external and internal standard method. In case of the first method, 8-point calibration curves were performed for each compound in the concentration range of 0–33 wt %. After the chromatographic analyses the mass balances for each synthesis were prepared.

The subsequent process functions were used to describe individual syntheses:

conversion of GA:

$$C_{GA} = \frac{\text{number of moles of reacted GA}}{\text{number of moles of introduced GA}} * 100 [\% \text{ mol}]$$

selectivity of LO,BP:

$$S_{LO,BP} = \frac{\text{number of moles of product "x"}}{\text{number of moles of reacted substrate "s"}} * 100 [\% \text{ mol}]$$

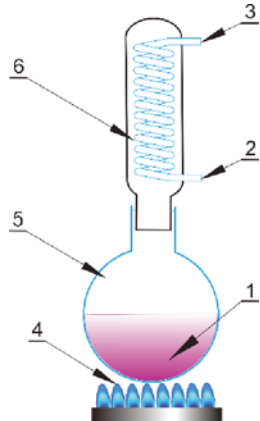


Figure 2. Scheme of the apparatus for carrying out the syntheses connected with the transformations of geraniol: 1 – reaction mixture, 2 – water outlet, 3 – water inlet, 4 – heating, 5 – round bottom flask, and 6 – reflux condenser

RESULTS AND DISCUSSION

Morphology of natural bentonite

Figure 3 shows an SEM image obtained for raw bentonite. As can be observed, the particles of this mineral are not interconnected. They form loose clumps with a variety of particle geometries. These observations have also been described by other authors²⁸.

The XRD spectrum (Fig. 4) shows that SiO₂ has the highest intensity among the compounds. These results

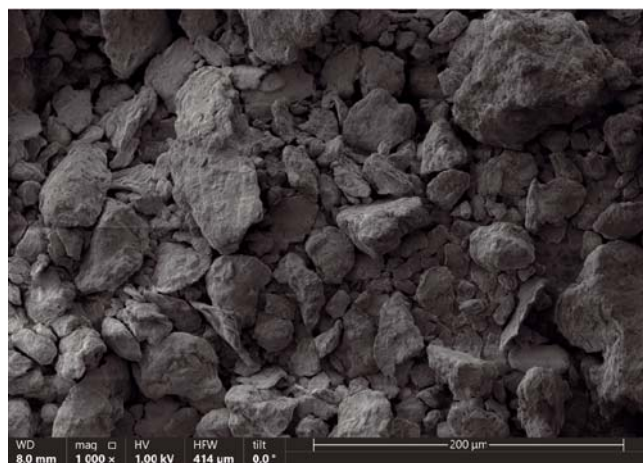


Figure 3. SEM images of natural bentonite

show that the bentonite used belongs to the group of aluminosilicates with characteristic reflections that occur at $2\theta = 27, 35, 43, 58$ and 63 . The diffractogram of bentonite has a similar pattern and is consistent with the spectra obtained by other authors²⁸.

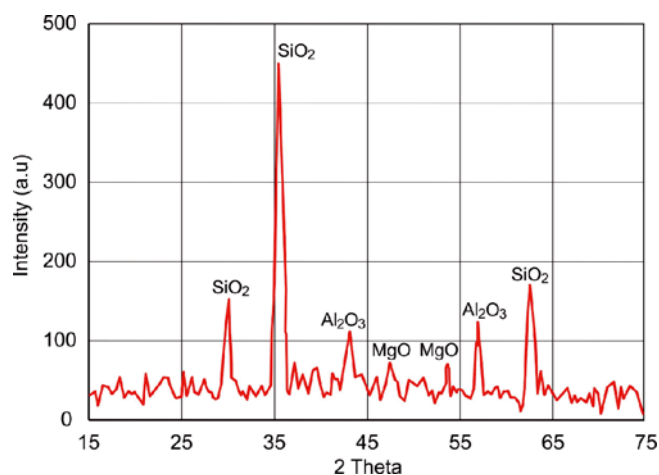


Figure 4. X-ray diffraction data for natural bentonite

Fig. 5 shows the FT-IR spectrum of the sample of natural bentonite. The adsorption bands at 467 cm^{-1} , 517 cm^{-1} , 783 cm^{-1} and 1120 cm^{-1} indicate the presence of quartz (SiO-Si), while the bands at 1034 cm^{-1} and 1634 cm^{-1} reveal the presence of amorphous SiO₂. The outlined bands at 617 cm^{-1} and 675 cm^{-1} refer to Al-O-Si-O bonding (presence of feldspar) and Al-Al-OH bonding at 917 cm^{-1} are also visible. The presence of -OH groups was confirmed by the presence of bands at 917 cm^{-1} , 3442 cm^{-1} and 3692 cm^{-1} . The spectrum obtained is consistent with the literature data²⁹.

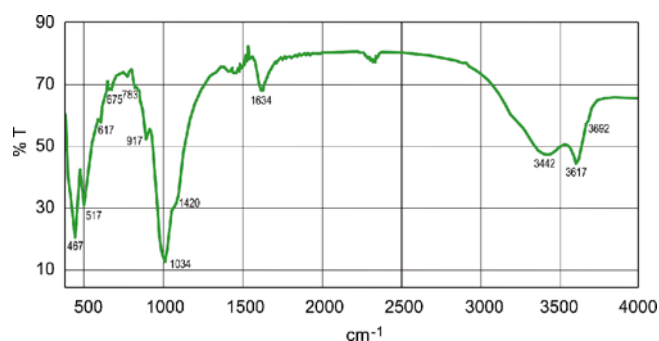


Figure 5. The FT-IR spectra of natural bentonite

The results of the elemental analysis for the tested catalyst are summarized in Table 1 and in Figure 6. For bentonite, the highest concentration was obtained for C (50.3 Atomic%), followed by O (42.1 Atomic%) and Si (3.8 Atomic%). In addition, the content of such elements as Mg, Na, Al and Fe was found. The results obtained are similar to those obtained by other authors²⁹.

Table 1. Results of EDXRF analysis

Element	Atomic %	Atomic % Error	Weight %	Weight % Error
C	50.3	0.2	40.6	0.2
O	42.1	0.2	45.3	0.2
Na	0.5	0.0	0.8	0.0
Mg	1.8	0.0	3.0	0.0
Al	1.3	0.0	2.3	0.0
Si	3.8	0.0	7.2	0.0
Fe	0.2	0.0	0.8	0.0

Figure 7 shows maps of the elements contained in natural bentonite. Seven major elements (silicon, carbon, oxygen, magnesium, aluminum, iron and sodium) were found in the case of the studied mineral. In all cases, an even distribution of elements on the surface of the mineral is evident.

Preliminary studies of the geraniol (GA) transformation process. The influence of temperature on GA transformation

Within the first parameter, the effect of temperature on the GA transformation process was studied. The temperature was studied in the range from 50 to 150 °C. The initial parameters were: catalyst content of 5 wt% and reaction time of 3 h. Figure 8 shows the effect of temperature on the function of GA conversion and on the selectivities of transformation to BP and LO. The GA conversion function tends to increase. It is initially about 30 mol% at 50 °C, and then increases to about 99 mol% at 80 °C. Above this temperature, chromatographic analysis showed the presence of only polymerization products. A similar increasing trend can be observed for the values of the functions of selectivity transformation to both BP and LO. In the case of BP, its selectivity values increase from about 3 mol% (50 °C) to about 21 mol% (80 °C). LO selectivity values increase from about 5 mol% (50 °C) to about 34 mol% (80 °C). Based on the tests, the temperature of 80 °C was selected as the most favorable temperature.

The influence of bentonite content on GA transformation

In the next step, the effect of the catalyst content (bentonite), in the range of 1.0 wt% to 10.0 wt%, on the GA conversion was checked. When the process is carried

out in the presence of bentonite, GA conversion remains high, and it changes from about 92 wt% (1.0 wt%) to about 100 mol% (10.0 wt%) (Fig. 9). The selectivity of transformation to BP decreases with increasing the amount of bentonite from about 30 mol% (1.0 wt%) to about 4 mol% (10.0 wt%). A similar pattern can be observed for LO, whose values of selectivity decreases from about 39 mol% (1.0 wt%) to about 6 mol% (10.0 wt%) (Fig. 9). The most preferred catalyst content for carrying out GA transformation in the presence of bentonite is the content of 1 wt%.

The influence of reaction time on GA transformation

The influence of reaction time on the course of GA transformation was investigated in the range from 15 min to 24 hours. The remaining parameters (temperature and reaction time) corresponded to the values previously determined as the most favorable. Figure 10 shows the changes the GA conversion function. During short reaction times, the conversion GA slowly increases from about 46 mol% (15 min) to about 61 mol% (60 min), followed by a significant increase: 91mol% – 120 min to 98 mol% – 1440 min. The values of the selectivity of transformation to BP in short reaction times increase from about 9 mol% (15 min) to about 30 mol% (180 min), followed by a sharp decrease to about 2 mol% (1440 min). A similar course is visible in the case of the selectivity of the transformation to LO. The values of this function initially increase to about 39 mol% (180 min) after which they decrease to about 17 mol% (1440 min). Considering the results obtained, the reaction time of 180 minutes was selected as the most favourable reaction time.

Optimization of geraniol transformation process parameters using Response Surface Method (RSM)

The method's control factors, such as temperature, catalyst content and reaction time, were selected based on preliminary studies. The control factors of the tests are shown in Table 2.

Table 2. Control parameters and values of process

Control parameters	Unit	Values		
		1	2	3
Temperature	[°C]	80	110	150
Catalyst content	[wt%]	1	5	10
Time	[h]	0.25	12	24

In order to reduce the number of tests and shorten testing time, the DOE (Design of Experiment) method was used. Tests were conducted in a manner consistent with a full factorial design. The response surface me-

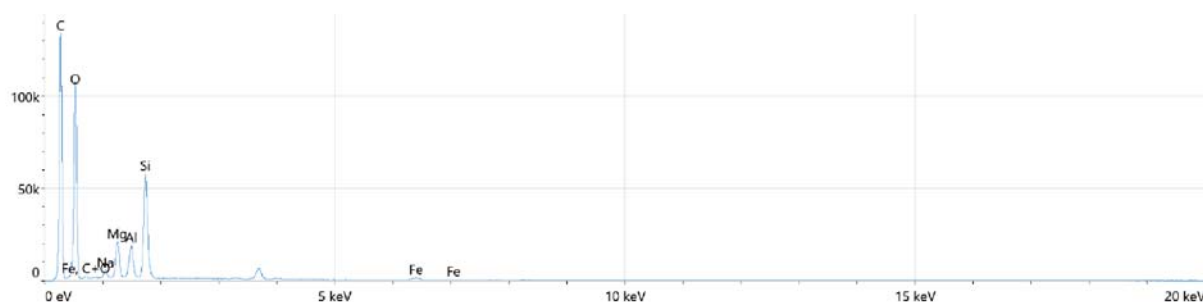


Figure 6. The XRF spectra of natural bentonite

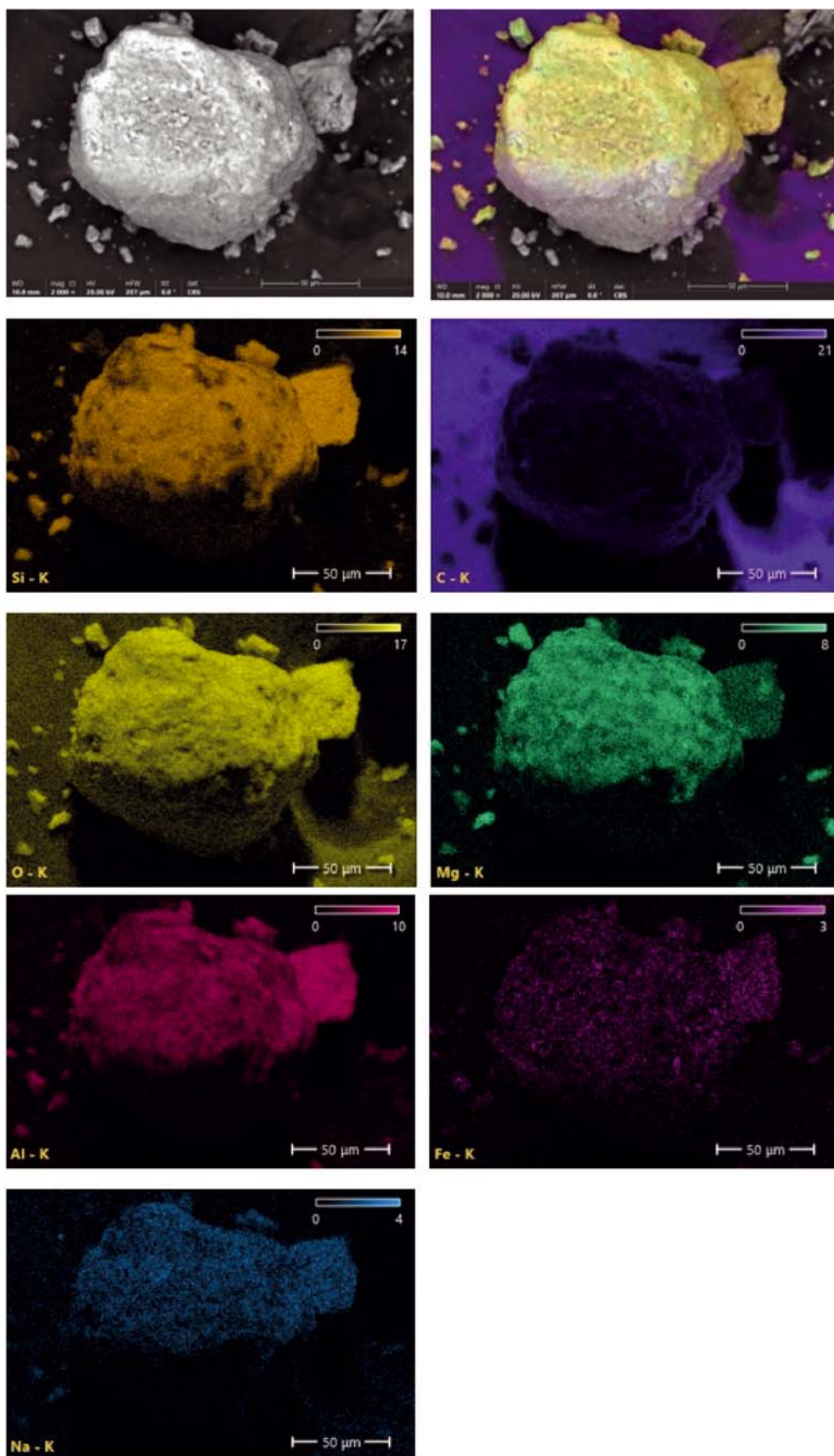


Figure 7. Element maps for natural bentonite

thod (RSM) with a central composite model was used. It consists of 27 experiments (Table 3).

A multinomial equation of second degree for determining the regression model value is:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 \pm \varepsilon$$

where:

y – is the dependent variable (response),
 x_i – indicates values of the i -th cutting parameter,
 $\beta_0, \beta_i, \beta_{ii}$ – are the coefficients of regressions,
 ε – is the error acquiring.

Statistica software was used to calculate the model equations. The results obtained for the effect of process control parameters (independent variables) on GA

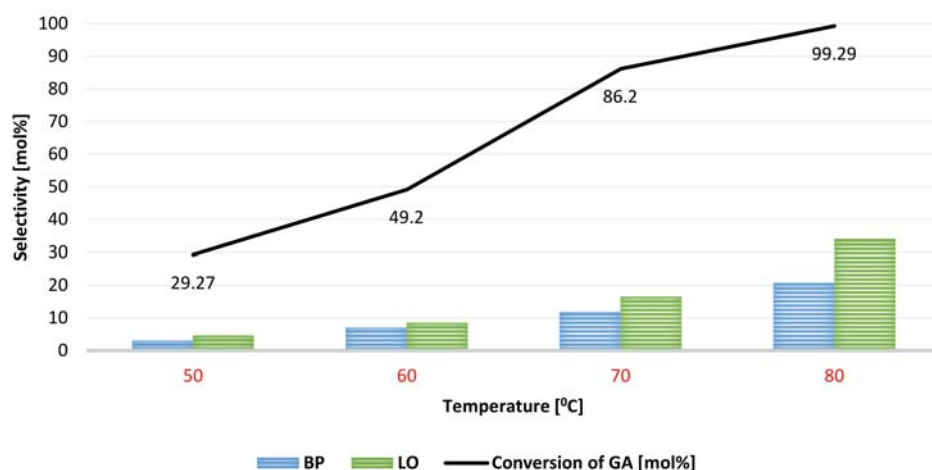


Figure 8. Effect of temperature on GA conversion function and selectivities of transformation to LO and BP in the presence of bentonite as the catalyst

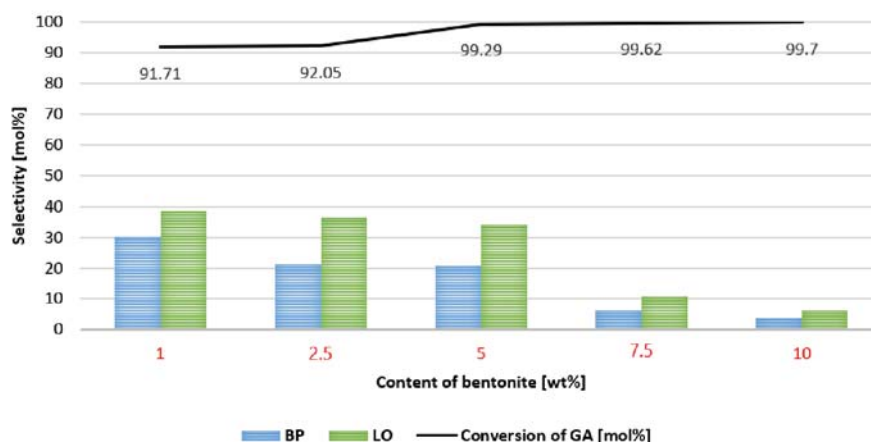


Figure 9. Effect of content of bentonite on GA conversion function and selectivities of transformation to LO and BP in the presence of bentonite as the catalyst

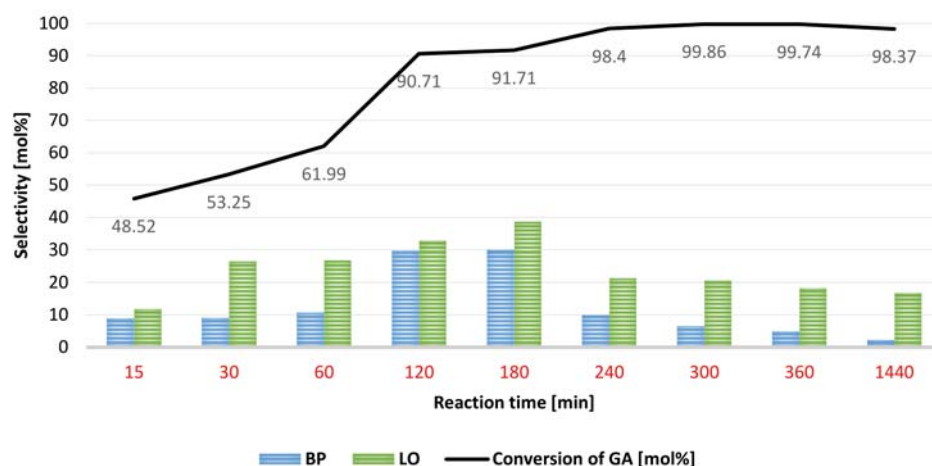


Figure 10. Effect of reaction time on GA conversion function and selectivities of transformation to LO and BP in the presence of bentonite as the catalyst

conversion and LO and BP selectivities (dependent variables) are summarized in Table 3. Columns 2 through 4 show the values of control factors (inputs) for the test process. Subsequent columns, 5 through 7, show the response values (output parameters).

Influence of process parameters on GA conversion

The particulars of GA conversion Analysis of Variance (ANOVA) for the 95% level of confidence ($\alpha = 0.05$)

was completed (Table 4). The model coefficient is statistically significant when it reaches P-Value < 0.05 . This is illustrated in Fig. 11.

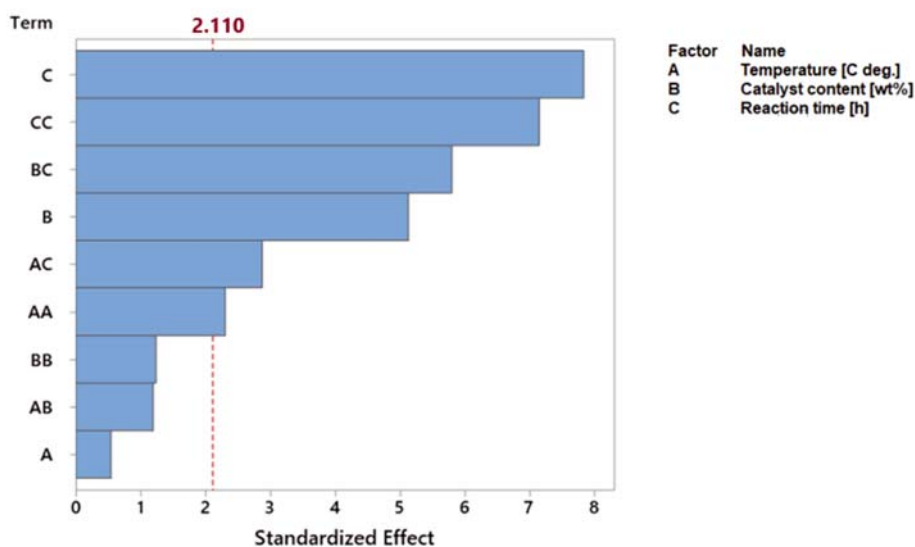
In order to roughly analyze multicollinearity, the variance increase factor (VIF) was determined. It calculates the strength of the multicollinearity phenomenon. The VIF shows how much the variance of the evaluated regression factor is inflated due to multicollinearity in the model. When the VIF is 1.0, multicollinearity

Table 3. Factors of the designed experiment

Test nr.	Temp	Bentonite content	Time	GA conversion	LO selectivity	BP selectivity
–	[°C]	[wt%]	[h]	[mol%]	[mol%]	[mol%]
1	80	1	0.25	68	12	17
2	80	1	12	92	15	20
3	80	1	24	93	16	22
4	80	5	0.25	78	19	24
5	80	5	12	95	25	30
6	80	5	24	92	26	32
7	80	10	0.25	86	26	37
8	80	10	12	97	33	39
9	80	10	24	96	31	36
10	110	1	0.25	76	19	24
11	110	1	12	95	26	31
12	110	1	24	92	26	32
13	110	5	0.25	84	29	34
14	110	5	12	98	32	38
15	110	5	24	96	30	34
16	110	10	0.25	95	37	48
17	110	10	12	95	33	45
18	110	10	24	92	31	46
19	150	1	0.25	75	26	23
20	150	1	12	94	23	30
21	150	1	24	90	23	30
22	150	5	0.25	82	26	31
23	150	5	12	96	30	32
24	150	5	24	93	30	32
25	150	10	0.25	93	32	45
26	150	10	12	93	29	43
27	150	10	24	88	29	43

Table 4. Analysis of Variance of GA conversion

Source	DF	Adj SS	Adj MS	F-Value	P-Value	VIF
Model	9	1432.39	159.154	21.77	9	1.01
Linear	3	642.44	214.146	29.29	3	1.01
Temperature [°C]	1	2.16	2.160	0.30	1	1.01
Catalyst content [wt%]	1	192.22	192.219	26.29	1	1.01
Time [h]	1	448.29	448.292	61.32	1	1.00
Square	3	423.54	141.178	19.31	3	1.00
Temperature [°C]*Temperature [°C]	1	38.92	38.920	5.32	1	1.01
Catalyst content [wt%]*Catalyst content [wt%]	1	11.22	11.221	1.53	1	1.00
Time [h]*Time [h]	1	373.39	373.394	51.08	1	1.00
2-Way Interaction	3	316.61	105.536	14.44	3	1.01
Temperature [°C]*Catalyst content [wt%]	1	10.41	10.411	1.42	1	1.01
Temperature [°C]*Time [h]	1	60.41	60.407	8.26	1	1.01
Catalyst content [wt%]*Time [h]	1	245.79	245.791	33.62	1	1.01
Error	17	124.28	7.311		17	1.01
Total	26	1556.67			26	1.01

**Figure 11.** Pareto chart of the standardized effects, Response is GA conversion [mol%], ($\alpha = 0.05$)

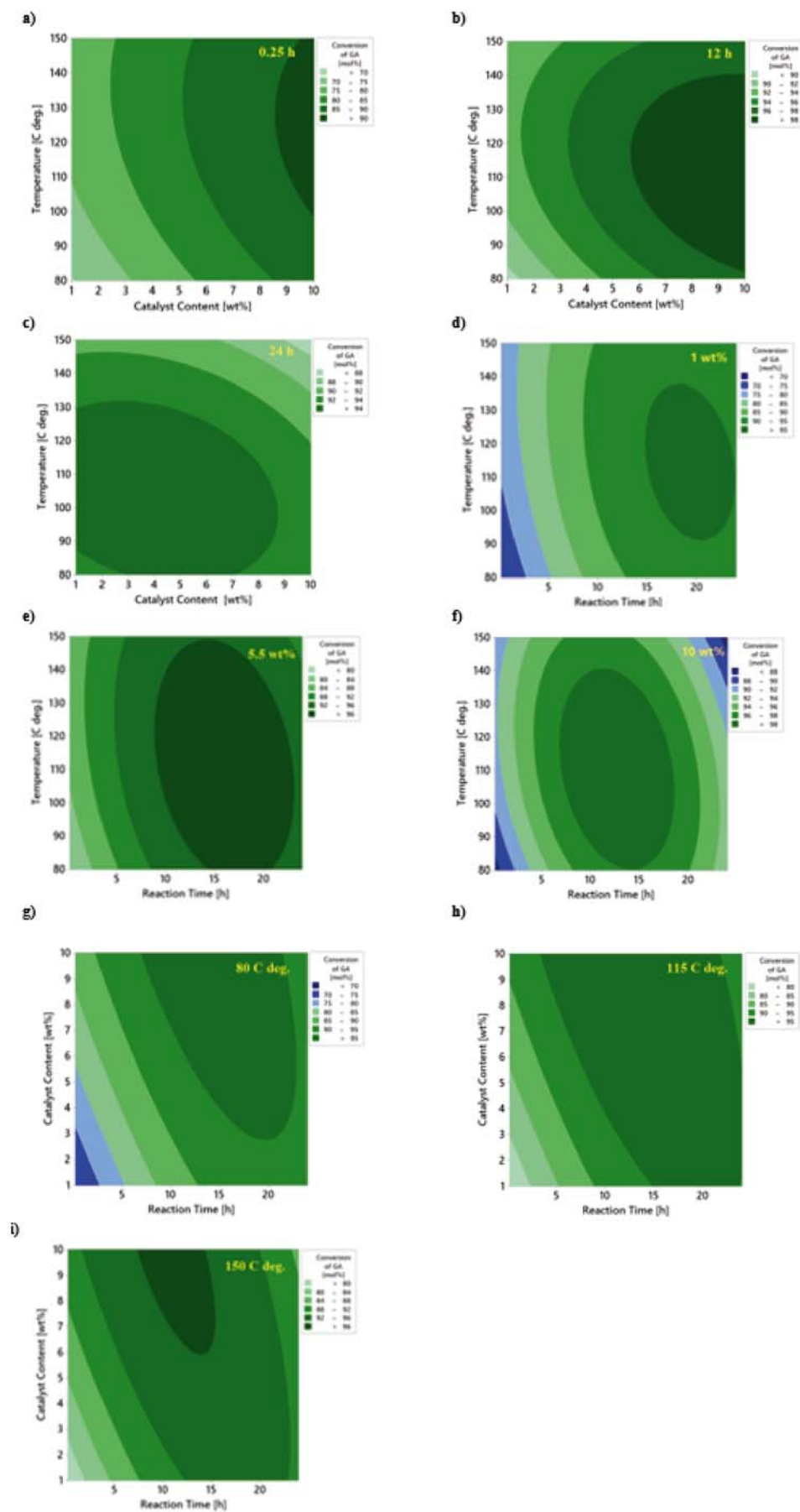


Figure 12. The influence of process parameters on geraniol conversion at: (a) 0.25 h, (b) 12 h, (c) 24 h, (d) 1 wt% catalyst content, (e) 5.5 wt% catalyst content, (f) 10 wt% catalyst content, (g) 80°C, (h) 115°C, (i) 150°C

is not present. For all analyzed factors, no significant multicollinearity was observed, as the VIF belongs to the interval $\{1, 1.01\}$.

Established on these effects the following calculation of GA conversion was required:

$$C_{GA} = 32,3 + 0,597T + 3,182C_c + 2,862t - 0,002130T^2 - 0,0685C_c^2 - 0,05595t^2 - 0,00588TC_c - 0,00538Tt - 0,0845C_c t$$

where:

C_{GA} – is geraniol conversion [mol%],

T – is temperature [°C],

C_c – is catalyst content [wt%],

t – is reaction time [min].

Figure 12 (a-i) shows the effect of the various parameters of the geraniol transformation process on GA conversion values. From the graphs below, it can be seen that as the catalyst content increases, the GA conversion values increase. A similar effect can be seen for temperature and reaction time. In the case of temperature, it can be seen that the GA conversion function reaches its maximum already in the range from 90 °C to 130 °C. In the case of the second parameter, reaction time, GA conversion reaches its optimum in the range from about 10 h to about 20 h. GA conversion reaches maximum values at > 98 mol%.

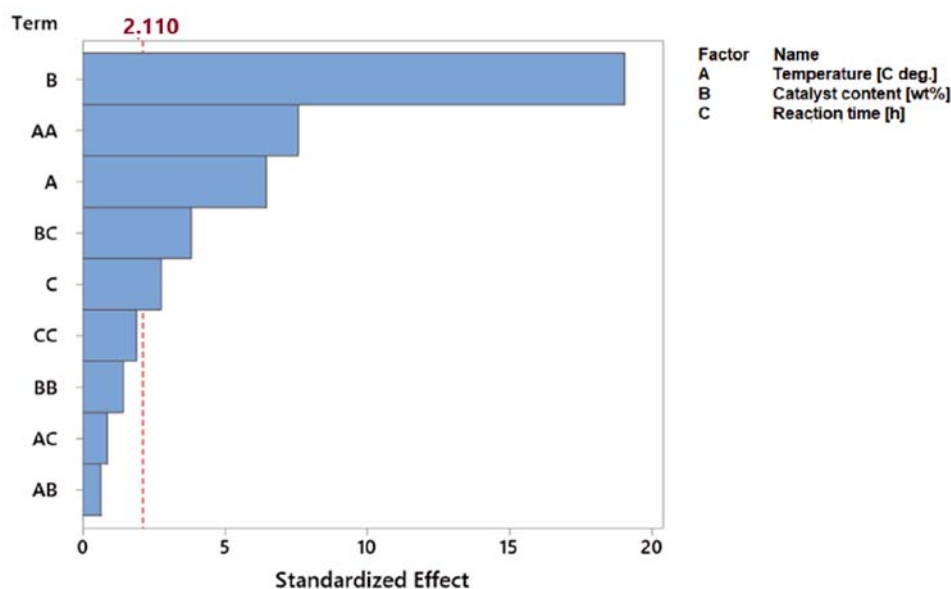


Figure 13. Pareto chart of the standardized effects, Response is BP selectivity [mol%], ($\alpha = 0.05$)

Table 5. Analysis of Variance of BP selectivity

Source	DF	Adj SS	Adj MS	F-Value	P-Value	VIF
Model	9	1754.71	194.97	54.1	0.000	1.01
Linear	3	1462.13	487.38	137.00	0.000	1.01
Temperature [°C]	1	148.41	148.41	41.72	0.000	1.01
Catalyst content [wt%]	1	1288.84	1288.84	362.30	0.000	1.01
Time [h]	1	27.26	27.26	7.66	0.013	1.00
Square	3	224.59	74.86	21.04	0.000	1.00
Temperature [°C]*Temperature [°C]	1	204.45	204.45	57.47	0.000	1.01
Catalyst content [wt%]*Catalyst content [wt%]	1	7.38	7.38	2.07	0.168	1.00
Time [h]*Time [h]	1	12.76	12.76	3.59	0.075	1.00
2-Way Interaction	3	56.26	18.75	5.27	0.009	1.01
Temperature [°C]*Catalyst content [wt%]	1	1.47	1.47	0.41	0.529	1.01
Temperature [°C]*Time [h]	1	2.69	2.69	0.76	0.397	1.01
Catalyst content [wt%]*Time [h]	1	52.10	52.10	14.65	0.001	1.01
Error	17	60.48	3.56			
Total	26	1815.19				

Influence of process parameters on BP selectivity

The particulars of BP selectivity Analysis of Variance (ANOVA) for the 95% level of confidence ($\alpha = 0.05$) was made (Table 5). The model coefficient is statistically significant when it reaches P-Value <0.05. This is illustrated in Fig. 13.

VIF reveals how much the variance of the evaluated regression factor is inflated as caused by multicollinearity in the model. For all tested factors, no significant multicollinearity was observed because VIF belongs to the range $\{1, 1.01\}$.

On basis research effects the following equation was defined:

$$C_{LO} = -53,0 + 1,061T + 4,272C_c + 0,805t - 0,003770T^2 - 0,1043C_c^2 - 0,00952t^2 - 0,01511TC_c - 0,00348Tt - 0,0198C_c t$$

where:

C_{BP} – is BP selectivity [mol%],

T – is temperature [°C],

C_c – is catalyst content [wt%],

t – is reaction time [min].

Figure 14 (a-i) shows the effect of process parameters on the BP selectivity values. In the case of reaction time and catalyst content, the function assumes optimum values in the upper ranges of the studied parameters. This is particularly evident in the case of catalyst content,

where the optimum is reached at a content of about 10 wt%. For temperature, the optimum is in the range of 110–130 °C. BP selectivity reaches maximum values at > 45 mol%.

Influence of process parameters on LO selectivity
The details of LO selectivity Analysis of Variance (ANOVA) for the 95% level of confidence ($\alpha = 0,05$) was completed (Table 6). The model coefficient is stati-

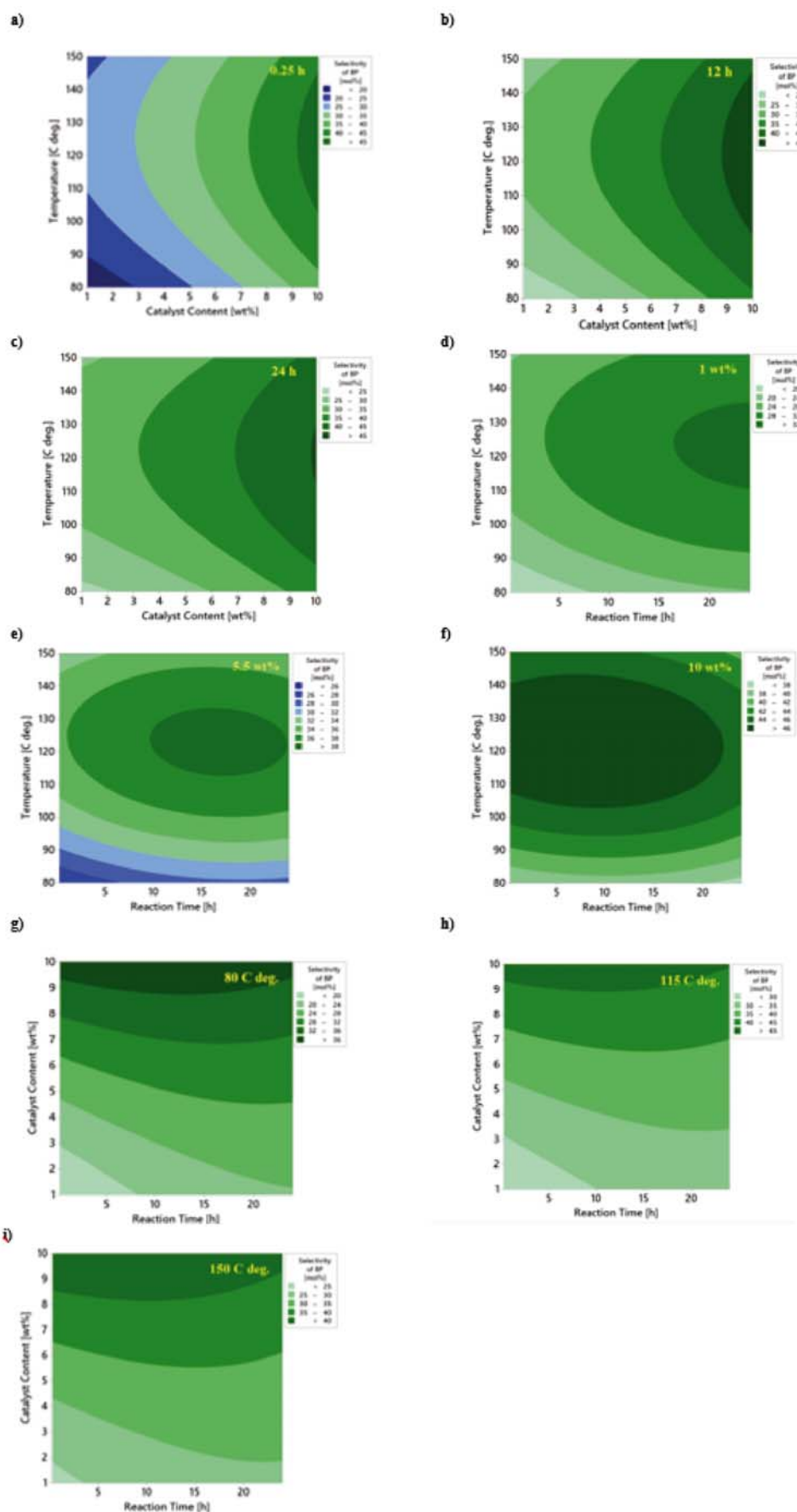


Figure 14. The influence of process parameters on BP selectivity at: (a) 0.25 h, (b) 12 h, (c) 24 h, (d) 1 wt% catalyst content, (e) 5.5 wt% catalyst content, (f) 10 wt% catalyst content, (g) 80 °C, (h) 115 °C, (i) 150 °C.

stically significant when it reaches P-Value <0,05, This is illustrated in Fig. 15. VIF reveals how much the variance of the evaluated regression factor is inflated as caused by multicollinearity in the model. For all tested factors, no significant multicollinearity was observed because VIF belongs to the range {1, 1,01}.

On basis research effects the following equation was designated:

$$C_{LO} = -53,0 + 1,061T + 4,272C_c + 0,805t - 0,003770T^2 - 0,1043C_c^2 - 0,00952t^2 - 0,015117C_c - 0,003487t - 0,0198C_c t$$

Where:

C_{LO} – is LO conversion [mol%],

T – is temperature [°C],

C_c – is catalyst content [wt%],

t – is reaction time [min].

Figure 16 a-i illustrates the effect of process parameters on LO selectivity values. In the case of temperature, the selectivity values increase with temperature, reaching the maximum in the range of 110–150 °C. In the case of the amount of catalyst, its increase also causes the increase in the values of the LO selectivity function. High values can be obtained in the range of catalyst steepness of 7–10 wt%. As can be seen, the reaction time of conducting the transformation process does not affect as significantly as the amount of catalyst. From the course of the curves it can be seen that the LO se-

lectivity reaches its optimum (>32 mol%) in the range from about 7 to about 20 h.

Composite desirability

The results of individual control parameters on all output parameters computed on ground the equation (3) and (4) are shown in Fig. 17. In addition, individual (for each output factor) and composite desirability were assessed. Individual and composite desirability estimate how well a variable fulfils the defined reaction targets.

Individual desirability (d) shown how the sets optimize a single response; composite desirability (D) appraises how the settings optimize a set of responses overall. Desirability has a range of 0 to 1. Value 0 represents the best event and value 1 shows that one or more responses are beyond their acceptable limits.

In this case, the composite desirability is equal 1 (or almost 1), which implies the settings appear to reach reasonable results for all responses. On this chart base, the optimum for all output parameters were specified. Best set of control parameters (temperature 120 °C, catalyst content 10.0 wt% and reaction time 9 h) indicating vertical red lines.

Table 6. Analysis of Variance of LO selectivity

Source	DF	Adj SS	Adj MS	F-Value	P-Value	VIF
Model	9	863.82	95.980	20.18	0.000	1.01
Linear	3	591.55	197.184	41.46	0.000	1.01
Temperature [°C]	1	104.05	104.054	21.88	0.000	1.01
Catalyst content [wt%]	1	477.79	477.785	100.47	0.000	1.01
Time [h]	1	10.92	10.918	2.30	0.148	1.00
Square	3	158.79	52.929	11.13	0.000	1.00
Temperature [°C]*Temperature [°C]	1	121.96	121.959	25.65	0.000	1.01
Catalyst content [wt%]*Catalyst content [wt%]	1	26.01	26.012	5.47	0.032	1.00
Time [h]*Time [h]	1	10.82	10.817	2.27	0.150	1.00
2-Way Interaction	3	107.38	35.792	7.53	0.002	1.01
Temperature [°C]*Catalyst content [wt%]	1	68.69	68.694	14.44	0.001	1.01
Temperature [°C]*Time [h]	1	25.23	25.231	5.31	0.034	1.01
Catalyst content [wt%]*Time [h]	1	13.45	13.451	2.83	0.111	1.01
Error	17	80.85	4.756			
Total	26	944.67				

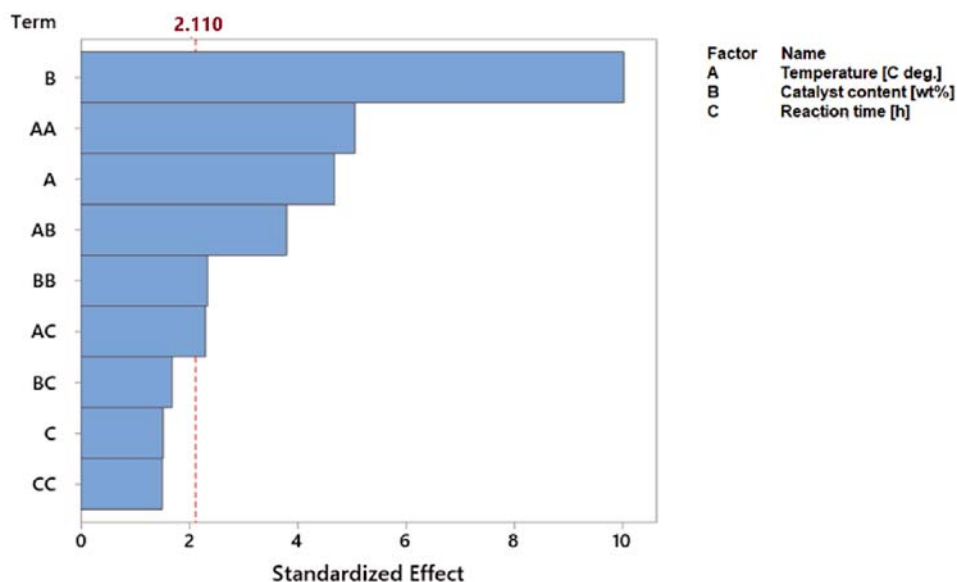


Figure 15. Pareto chart of the standardized effects, Response is LO selectivity [mol%], ($\alpha = 0.05$)

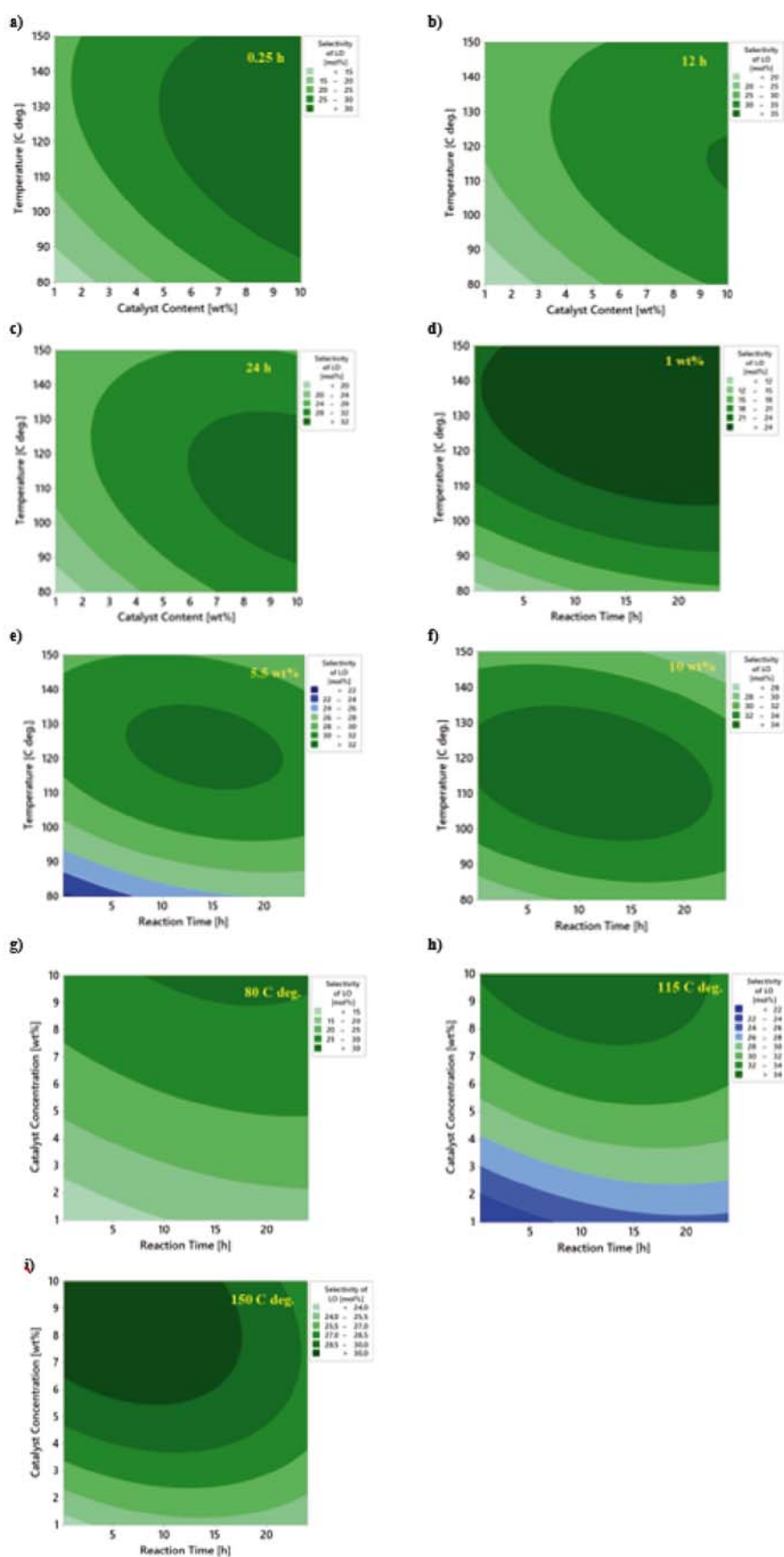


Figure 16. The influence of transformation process parameters on LO selectivity at: (a) 0.25 h, (b) 12 h, (c) 24 h, (d) 1 wt% catalyst content, (e) 5.5 wt% catalyst content, (f) 10 wt% catalyst content, (g) 80 °C, (h) 115 °C, (i) 150 °C

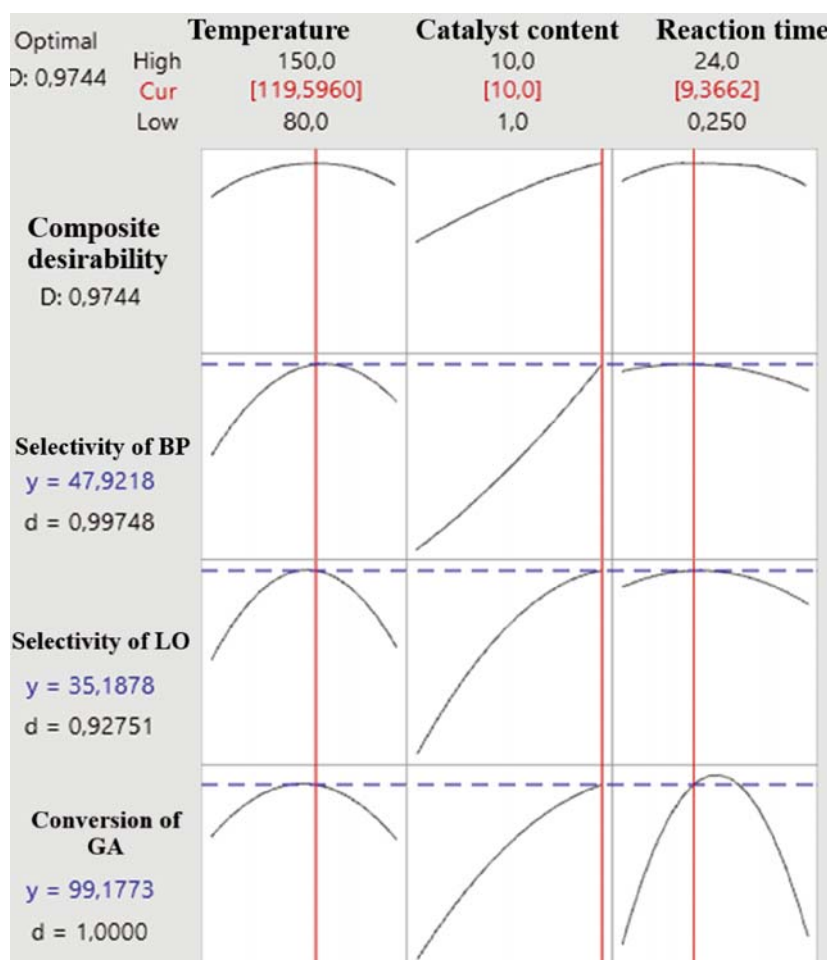


Figure 17. Combination of control parameter values at optimal condition for all output parameters

CONCLUSIONS

The application of the Surface Response Method for organic compounds synthesis optimization process allows to determine the process parameters, which significantly affect the course of the research process while allowing the user to ignore those factors that have negligible effect on the results. Optimization of these process parameters made it possible to determine the sets of technological parameters in which the tested functions obtain their maximum values and to determine the interaction between these parameters. The research conducted is entitled to draw the following conclusions:

For GA conversion, the optimum was achieved 98 mol% for the following control parameters: temperature 110 °C, catalyst content 5.0 wt% and reaction time 12 h.

Optimum is reached for BP selectivity 48 mol% for the following control parameters: 110 °C, catalyst content 10.0 wt% and reaction time almost 0.25 h.

For the selectivity of LO, the optimum was achieved 37 mol% at the following control parameters: temperature 110 °C, catalyst content 10.0 wt% and reaction time almost 0.25 h.

The optimum set of control parameters of the process for all output parameters are following: temperature 120 °C, catalyst content 10.0 wt% and process time 9 h.

Comparing the results obtained with those from preliminary tests, it was observed that the temperature value increased from 80 to 120 °C under optimal conditions. A similar trend was observed in the case of catalyst content, where there was a tenfold increase in

the amount of catalyst from 1 to 10 wt%. Also in the case of reaction time, the increase can be seen from 3 h to more than 9 h. However, the value of the selectivity of the transformation to BP increased from 39 mol% (preliminary studies) to about 48 mol% (model studies). The selectivity of transformation to LO also increased from 30 mol% (preliminary studies) to 35 mol% (model studies). GA conversion values in preliminary studies were about 92 mol% while in model studies they were 99 mol%. Nevertheless, using process optimization, the testing process can be simplified, reducing the time to obtain reliable results and lowering the cost of testing by reducing the number of tests required. Regardless, according to the method described, the testing process can be simplified, again reducing the time to obtain reliable results and lowering the cost of testing by reducing the number of tests required (Table 7).

Table 7. The comparison of the values of the most favorable parameters of the GA transformation process in the presence of bentonite obtained from preliminary and model tests

	Experimental value	Modeling value
Temperature (°C)	80	120
Bentonite content (wt%)	1	10
Reaction time (min)	3	>9
Conversion of geraniol	$C_{GA} = 91.71$ mol%	$C_{GA} = 99.18$ mol%
The obtained values of selectivity of transformations to individual reaction products	$S_{BP} = 38.63$ mol% $S_{LO} = 38.63$ mol%	$S_{BP} = 47.92$ mol% $S_{LO} = 38.63$ mol%
GA – geraniol, BP – beta-pinen, LO – linalol		

In the future, new research areas related to the isomerization of geraniol may focus on the exploration of various natural materials with porous structures. Additional potential research directions in this process include controlled pressure alterations (utilizing an autoclave with a Teflon liner for high-pressure processes) and the development of optimal solvents.

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