



Optimization of biodiesel production from corn oil by methanolysis catalyzed by corn cob ash

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ABSTRACT

The use of low-cost or priceless feedstocks such as byproducts in biodiesel production results in a reduced overall process costs. The present paper reports the use of corn germs and corn cobs as byproducts from corn-based starch production in the biodiesel production by the methanolysis of the oil extracted from corn germs, catalyzed by the ash produced by combustion of corn cobs. The major aim was to optimize the methanol-to-oil molar ratio, catalyst loading, and reaction time in a batch stirred reactor with respect to the content of methyl ester fatty acids (FAME). The statistical modeling and optimization were carried out using a second-order polynomial (quadratic) model developed by the response surface methodology combined with a 3³ factorial design with 3 central points. The FAME content was determined by a high-pressure liquid chromatography method. The analysis of variance showed that only the catalyst amount, the reaction time, the catalyst amount interaction with reaction time and all three quadratic terms were the significant model terms with the confidence level of 95 %. The optimum reaction conditions (the catalyst amounts of 19.8 %, the methanol-to-oil molar ratio of 9.4 mol/mol and the reaction time of 31 min) provided the FAME content of 98.1 %, which was in an excellent agreement with the predicted FAME content (98.4 %). Thus, both corn germs and corn cobs may be suitable feedstocks for biodiesel production.

1. Introduction

Biodiesel, a mixture of fatty acid alkyl esters (FAAE) that satisfy the prescribed standards, such as EN14240, is commonly produced by esterification of free fatty acids (FFAs) and/or transesterification (alcoholysis) of triacylglycerols (TAG) from various renewable bioresources with methanol or ethanol, in the presence of a catalyst. Because of its growing use (Živković et al.,

2017) and almost unchangeable price (Veljković et al., 2018), biodiesel production is expected to expand from $29.7 \cdot 10^6 \text{ m}^3$ in 2014 to $39 \cdot 10^6 \text{ m}^3$ in 2024, which is a 27 % increase (OECD/FAO, 2015). The main feedstocks for biodiesel production are oil crops like rapeseed, soybean, and palm oils, which mainly contribute to the high biodiesel production price. Therefore, other oil crops that could grow on marginal lands and produce non-edible oils should be looked for. Besides that, low-

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cost or priceless by-products and wastes of existing production processes, which contains oil, are also interesting as biodiesel feedstocks. Such by-products are, for instance, corn germ in starch production and distillers dry grains with solubles (a part of whole stillage) in ethanol production (Noureddini et al., 2009; Moser and Vaughn, 2012).

So far, corn oil has not been a feasible biodiesel feedstock because of its high value as edible oil and relatively high price despite its huge global production (about 3.2 million tons) (FAO, 2016). However, being a by-product from ethanol or starch production, corn oil is the fastest expanding biodiesel feedstock because its use had increased about ten-fold from 2010 to 2015 (Veljković et al., 2018). The transesterification reaction is most frequently used for the conversion of corn oil-based feedstocks into biodiesel (Veljković et al., 2018).

The transesterification reactions of corn oil over heterogeneous base catalysts are reviewed in Table 1. MgO, ZnO, Ba(OH)₂, ZnAl₂O₄, KOH, loaded CaO on silica or alumina, and CaO from snail shells have been used as a solid catalyst, while methanol, ethanol, and dimethyl carbonate have been applied as acyl acceptors. Except for the reaction with ZnAl₂O₄, the other reactions were conducted at the temperature lower than the boiling point of the acyl acceptor. The highest ester yield (> 96 %) has been obtained from neat and waste frying corn oil with Ba(OH)₂ and CaO from snail shells within 2 and 1 h, respectively. The use of cheap but active catalysts is another way to reduce the overall biodiesel production costs, such as ashes generated by combustion of

agricultural wastes (Basumatary et al., 2018).

Corn cob ash has been used for preparing silica-based catalysts with potential for complete removal of methylene blue (Velmurugan et al., 2015) or hydrogenation of lignin-derived alkylphenols (Salakhum et al., 2018), but it has not been applied yet as a catalyst in biodiesel production.

The efficiency of biodiesel production processes, leading to the reduction of the production costs, can also be increased by conducting them under the optimum reaction conditions, which are usually determined using the response surface methodology (RSM) in combination with a design of experiment (DoE). This approach has widely been used in recent years for the improvement of the biodiesel production from corn oil. For this purpose, the RSM is usually combined with full factorial (Fernandes et al., 2012; de Lima et al., 2013), central composite (El Boulifi et al., 2010; Ciftci and Temelli, 2011; Moradi et al., 2014; Mustata and Bicu, 2014) or Box-Behnken (Sun et al., 2014) design.

A review of the literature regarding statistical modeling and optimization of biodiesel production from corn oil-based feedstocks are given in Table 2. The present paper deals with the biodiesel production by methanolysis of the oil extracted from corn germs in the presence of the ash produced by combustion of corn cobs; both corn germs and corn cobs are byproducts from corn-based starch production. The major goal of the study is the optimization of the reaction conditions with respect to the methanol-to-oil molar ratio, catalyst loading, and reaction time.

Table 1

A review of the transesterification reactions of corn oil over heterogeneous base catalysts

Catalyst / loading, % to the oil	Type of acyl acceptor	Acyl acceptor:oil molar ratio, mol/mol	Tempe- rature, °C	Type, volume of reactor, mL / Type of stirrer, stirring rate, rpm	Optimal reaction conditions		Reference
					Reaction conditions	Yield (Conversion), % / Time, h	
ZnAl ₂ O ₄ / –	Methanol	12:1	150–200	Batch reactor – / – 800 (500 kPa)	150 °C	(22.7) / 2	Velázquez, (2007)
MgO / 2–9	Ethanol Methanol	10:1 – 30:1	65	Flask, 150 / magnetic, 800	200 °C 20:1, 5 %	(32.5) / 2 62.61 / 10	Hatefi et al., (2014)
ZnO / 2–11					15:1, 9 %	53.1 / 10	
CaO/SiO ₂ / 6	Methanol	16:1	50–65	Flask, 250 / –, 600	60 °C	(85.6) / 8	Moradi et al., (2014)
CaO/γ–Al ₂ O ₃ / 6	Methanol	12:1	65	Flask, 250 / –		79.1 / 5	Moradi et al., (2015)
CaO/γ–Al ₂ O ₃ / 1–5	Methanol	6:1–12:1	20–65	Flask, 250 / magnetic, 900	12:1, 5 %, 65 °C	(91.58) / 6	Waisi et al., (2015)
Ba(OH) ₂ / 1.76–4.24	Methanol	5.4:1 – 12.6:1	33	Vessel, 500 / mechanical, 500	11.32:1, 3.6 %	99.15 ^a / 2	Mustata and Bicu, (2014)
CaO from snails shells ^a / 3–9	Methanol	6:1–12:1	60	Flask, 250 / magnetic, 200	6:1, 3 %	96 / 1	El-Gendy et al., (2014)
CaO / 3 %		6:1			–	95 / 1	
KOH / 10–20	Dimethyl carbonate	3:1 – 9:1	65–75	Flask, – / magnetic, –	9:1, 16.3 %, 60 °C	90.9 / 9	Sun et al., (2014)

^a Waste frying corn oil

Table 2
The review of the literature regarding to statistical modeling and optimization of biodiesel production from corn oil-based feedstocks

Feedstock ^a	WFCO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO	CO
Acyl acceptor ^b	MeOH	MeOH	DMC	MeOH	MeOH	MeOH	MeOH	MeOH	EtOH	EtOH	EtOH	EtOH
Catalyst ^c	CaO	CaO/silica	KOH	Ba(OH) ₂	Lipase	KOH	KOH	NaOH	NaOH	NaOH	NaOH, KOH	NaOH, KOH
Design of experiments ^d	D-OD	BBD	BBD	CCD	CCD	BBD	CCD	FFD	FFD	FFD	FFD	CCD
Number of factors	4	3	3	3	4	3	2	2	2	2	6	2
Number of levels	3	3	3	5	5	3	2	5	3	3	2	5
Response ^e	EY	EP	EY	EY	EP	EY	EY	EY	EP	EP	EY	EY
Reaction temperature (A)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Molar ratio (B)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Catalyst amount (C)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Reaction time (D)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Stirring speed (E)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Pressure (F)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CO ₂ flow rate (G)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Influential factors ^f	B, C, D, B ² , C ²	C, E, C ²	C, E, C ²	B, C, B ² , C ²	A, B, A ²	ng ^g	A, C, A·C	A, C, A·C	B, C, C ²	B, C, C ²	To screen factors	ng
Reference	El-Gendy et al., (2014)	Moradi et al., (2014)	Mustata and Bicu, (2014)	Sun et al., (2014)	Ciftci and Temelli, (2011)	El Boulifi et al., (2010)	Fernandes et al., (2012)	de Lima et al., (2013)				

^a CO – corn oil and WFCO – waste frying corn oil. ^b MeOH – methanol, EtOH – ethanol and DMC – dimethyl carbonate. ^c IL – ionic liquid. ^d FFD – full factorial design, fFD – fractional factorial design, D-OD – D-optimal design, BBD – Box-Behnken design and CCD – central composite design. ^e EP – esters purity and EY – esters yield. ^f At the 95% confidence level. ^g ng – not given.

2. Experimental

2.1. Materials

Corn germs, with a moisture content of 3.3 %, were purchased from the ALMEX-IPOK, Zrenjanin, Serbia. Corn germs were ground in a Braun electric grinder for 2 min and sieved through a 0.8 mm screen. The oil was extracted from the ground germs using *n*-hexane. Waste corn cobs were combusted in an oven and the obtained ash was used as a catalyst. Methanol (99.5 %, Zorka-Pharma, Serbia and HPLC grade, Promochem LGC, Germany), *n*-hexane (HPLC grade, Promochem LGC, Germany) and 2-propanol (HPLC grade Carlo Erba, Italy) were used.

2.2. Extraction of oil by maceration

The oil was also extracted from the ground corn germs by maceration. Ground corn germs (200 g) and *n*-hexane (600 ml) were poured into an Erlenmeyer (1000 ml), equipped with a reverse condenser, which was then kept for 15 min in a water bath at 20 °C. After completion of the extraction, the liquid extract was separated from the residual solid material by filtration using a Büchner funnel. The cake obtained after filtration was washed with 200 ml of *n*-hexane. Thereafter, the combined filtrate was evaporated at 50 °C to a constant mass using the rotary vacuum evaporator.

2.3. Methanolysis of corn oil

The base-catalyzed methanolysis of the corn oil obtained by maceration was carried out in a three-necked round-bottom flask (250 ml), equipped with a reflux condenser and a magnetic stirrer, which was placed in a thermostated water bath. The reaction was carried out at the methanol-to-oil molar ratio of 9:1, 12:1 or 15:1, the catalyst concentration of 10, 15 or 20 % (based on oil mass), and 60 °C under atmospheric pressure.

The oil (20 g) and the appropriate amounts of catalyst and methanol were added to the reaction flask and stirred

with a magnetic stirrer (900 rpm). The catalyst particles were uniformly distributed in the liquid. At different time intervals during the reaction, samples (0.5 ml) of the reaction mixture were taken to determine the conversion of TAG. The samples were centrifuged (Sigma, Germany) at 3500 min⁻¹ (average 700 ×g) for 10 min to separate the ester-oily and alcoholic phases. The upper ester-oil layer was separated and dissolved in a mixture of 2-propanol and *n*-hexane (5:4 v/v) in a ratio of 1:200, and then filtered through a Millipore (0.45 μm) filter for quantitative analysis using an HPLC method (Stamenković et al., 2007). The TAG conversion degree (x_A) was calculated on the basis of the actual and initial TAG contents in the oily-ester phase of the reaction mixture using the following equation:

$$x_A = 1 - TAG / TAG_0 \quad (1)$$

where *TAG* and *TAG*₀ are the actual and initial concentration of TAG (%).

2.4. Modeling the experimental results of the methanolysis reaction

The methanolysis of corn oil was investigated at various amounts of catalyst (factor A), methanol-to-oil molar ratios (factor B) and reaction times (factor C) according to a 3³ factorial design with 3 central points.

The dependent variable (response) was the FAME content in the oily-ester phase of the reaction mixture.

The lower, central and upper coded values of the process factors are designated as (-1), (0) and (1), respectively. The values of the coded and non-coded process factors are shown in Table 3. In order to minimize the error, the experiments were performed in a random order.

The obtained experimental data of the FAME content were modeled by the non-linear regression method using the second-order polynomial equation (Eq. 2), which correlated the dependent variable with the process factors:

$$y = b_0 + b_1A + b_2B + b_3C + b_{12}AB + b_{13}AC + b_{23}BC + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 \quad (2)$$

where *y* is FAME content, *A*, *B* and *C* are factors, *b*₀ is the regression coefficient, *b*_{*i*}, *b*_{*ii*}, and *b*_{*ij*} (*i*, *j* = 1, 2, 3) are linear, quadratic, and two-way interaction regression coefficients, respectively. The complete design matrix of the 3³ factorial design with 3 central points is shown in Table 4, consisted of 30 experimental runs. According to the Kolmogorov-Smirnov normality test, the FAME content data were normally distributed at the 0.05 level of significance.

The obtained experimental data were analyzed by the

R-Project software (open source, <http://cran.us.r-project.org>). Statistical significance of the process factors and their interactions, as well as the applicability of the model, was assessed by the analysis of variance (ANOVA). The influence of the process factors on FAME content was analyzed using the RSM, while the optimal conditions providing the maximum FAME content were determined by solving the regression equation.

Table 3
Process factors

Symbol	Factor	Unit	Level		
			(-1)	(0)	(+1)
A	Catalyst (ash) amount	% ^a	10	15	20
B	Methanol-to-oil molar ratio	mol/mol	9:1	12:1	15:1
C	Reaction time	min	20	30	40

^a Based on the oil mass**Table 4**
Experimental matrix of the 3³ factorial design with 3 central points

Run	Coded factors			Uncoded factors			FAME, Y (%)		
	Factor A	Factor B	Factor C	Factor A	Factor B	Factor C	Actual	Predicted	Relative deviation ^a (%)
1	-1	-1	-1	10	9	20	11.1	8.3	25.2
2	0	-1	-1	15	9	20	42.3	54.3	-28.4
3	1	-1	-1	20	9	20	91.2	81.2	11.0
4	-1	0	-1	10	12	20	17.7	13.6	23.2
5	0	0	-1	15	12	20	59.4	56.03	5.7
6	1	0	-1	20	12	20	73.9	79.2	-7.2
7	-1	1	-1	10	15	20	12.0	5.5	54.2
8	0	1	-1	15	15	20	33.9	44.2	-30.4
9	1	1	-1	20	15	20	64.7	63.8	1.4
10	-1	-1	0	10	9	30	37.6	44.5	-18.4
11	0	-1	0	15	9	30	82.4	81.6	1.0
12	1	-1	0	20	9	30	98.0	99.6	-1.6
13	-1	0	0	10	12	30	44.5	52.5	-18.0
14	0	0	0	15	12	30	96.1	86.0	10.5
15	1	0	0	20	12	30	96.5	100.3	-3.9
16	-1	1	0	10	15	30	43.3	47.0	-8.5
17	0	1	0	15	15	30	77.9	76.9	1.3
18	1	1	0	20	15	30	90.1	87.6	2.8
19	-1	-1	1	10	9	40	69.1	62.5	9.6
20	0	-1	1	15	9	40	92.0	90.7	1.4
21	1	-1	1	20	9	40	98.8	99.8	-1.0
22	-1	0	1	10	12	40	71.0	73.1	-3.0
23	0	0	1	15	12	40	96.6	97.8	-1.2
24	1	0	1	20	12	40	96.5	103.2	-6.9
25	-1	1	1	10	15	40	71.0	70.4	0.8
26	0	1	1	15	15	40	88.9	91.4	-2.8
27	1	1	1	20	15	40	98.2	93.2	5.1
28	0	0	0	15	12	30	80.1	86.0	-7.4
29	0	0	0	15	12	30	94.5	86.0	9.0
30	0	0	0	15	12	30	93.0	86.0	7.5

MRPD^b (%) = ±10.3^a Relative deviation (%) = (Actual – Predicted) 100/Actual. ^b MRPD = $\sum |Relative\ deviation| / n$, where $n = 30$

3. Results and discussion

3.1. Development and assessment of the statistical model

First, the adequacy of the possible statistical models was checked by (a) sequential sum of squares, (b) lack of fit and (c) model summary statistic tests. They select the highest order non-aliased polynomial model where the additional terms are significant, the model with insignificant lack of fit and the model maximizing the R^2_{adj} and the R^2_{pred} , respectively. These tests suggested disregarding the cubic models as being aliased (Tables 5-7). Excluding the aliased cubic models, the quadratic model had the highest R^2 -value (0.956) among the tested models. This high R^2 -value implied the acceptable goodness of fit of the quadratic model. Besides that, the R^2_{pred} -value of 0.895 was in reasonable agreement with the R^2_{adj} -value of 0.936, indicating no problem with the developed model and/or data. Indeed, no outlier was

observed in the tested dataset. Moreover, the lack of fit for the quadratic model was insignificant relative to pure error, which confirmed that this model fitted the data well.

Therefore, the quadratic model was accepted for modeling FAME content with the process factors. The ANOVA results are shown in Table 8. The F_{model} - and p -values implied the model was significant, meaning that the model fitted well. The same conclusion was supported by the relatively low $MRPD$ -values ($\pm 10.3\%$, 14 data, Table 4).

According to the ANOVA result, the catalyst amount (A), the reaction time (C), the catalyst amount interaction with reaction time ($A \times C$) and all three quadratic terms (A^2 , B^2 and C^2) were the significant model terms with the confidence level of 95%. On the other hand, the effect of the methanol-to-oil molar ratio (B) and its interactions with the other two process factors ($A \times B$ and $B \times C$) on FAME content were statistically insignificant with the confidence level of 95%.

Table 5

Results of sequential model sum of squares test

Source	Sum of squares	df	Mean square	F-value	p-value	Remark
Mean vs Total	150,138.6	1	150,138.6			
Linear vs Mean	18,251.3	3	6,083.8	36.90	< 0.0001	
Two-factor interaction vs Linear	1,191.1	3	397.0	2.95	0.054	
Quadratic vs 2FI	2,098.0	3	699.3	14.02	< 0.0001	Suggested
Cubic vs Quadratic	283.9	7	40.6	0.74	0.644	Aliased
Residual	713.6	13	54.9			
Total	172,676.4	30	5,755.9			

Table 6

Results of lack of fit test

Source	Sum of squares	df	Mean square	F-value	p-value	Remark
Linear	4,125.5	23	179.4	3.34	0.175	
Two-factor interaction	2,934.4	20	146.7	2.73	0.222	
Quadratic	836.5	17	49.2	0.92	0.620	Suggested
Cubic	552.6	10	55.3	1.03	0.556	Aliased
Pure Error	161.0	3	53.7			

Table 7

Results of model summary statistics test

Source	Stand. dev.	R^2	R^2_{adj}	R^2_{pred}	
Linear	12.84	0.810	0.788	0.754	
Two-factor interaction	11.60	0.863	0.827	0.795	
Quadratic	7.06	0.956	0.936	0.895	Suggested
Cubic	7.41	0.968	0.929	0.763	Aliased

Table 8
ANOVA results for the quadratic model

Source	Sum of squares	df	Mean square	F-value	p-value
Model	21,540.3	9	2,393.4	47.99	< 0.0001
<i>A</i>	10,300.9	1	10,300.9	206.53	< 0.0001
<i>B</i>	100.3	1	100.3	2.01	0.172
<i>C</i>	7,850.0	1	7,850.0	157.39	< 0.0001
<i>AxB</i>	157.7	1	157.7	3.16	0.091
<i>AxC</i>	947.0	1	947.0	18.99	0.0003
<i>BxC</i>	86.4	1	86.4	1.73	0.203
<i>A</i> ²	633.3	1	633.3	12.70	0.002
<i>B</i> ²	310.3	1	310.3	6.22	0.022
<i>C</i> ²	567.1	1	567.1	11.37	0.003
Residual	997.5	20	49.9		
Lack of Fit	836.5	17	49.2	0.92	0.620
Pure Error	161.0	3	53.7		
Corrected Total	22,537.8	29			

The quadratic model is as follows:

- Coded factors

$$y = 86.00 + 23.92A - 2.36B + 20.88C - 3.62AB - 8.88AC + 2.68BC - 9.61A^2 - 6.73B^2 - 9.09C^2 \quad (3)$$

- Uncoded (actual) factors

$$y = -406.20 + 24.55A + 18.09B + 9.14C - 0.24AB - 0.18AC + 0.09BC - 0.38A^2 - 0.75B^2 - 0.09C^2 \quad (4)$$

After eliminating the insignificant terms, Eqs (3) and (4) become the reduced quadratic models as follows:

- Coded factors

$$y = 86.00 + 23.92A - 2.36B + 20.88C - 8.88AC - 9.61A^2 - 6.73B^2 - 9.09C^2 \quad (5)$$

- Uncoded (actual) factors

$$y = -394.89 + 22.65A + 17.15B + 10.21C - 0.18AC - 0.38A^2 - 0.75B^2 - 0.09C^2 \quad (6)$$

The R^2 -value (0.945) demonstrated a good fitting capability of the reduced quadratic model, which was supported by an acceptable *MRPD*-value ($\pm 10.6\%$, 30 data). In addition, the R^2_{adj} - and R^2_{pred} -values (0.927 and 0.896, respectively) were high and close enough to each other, implying that the reduced quadratic model represented the experimental data well. This reduced quadratic model was further used for response surface analysis and optimization.

3.2. Response surface analysis and optimization

Figure 1 shows the response surface 3D plots for FAME content as a function of catalyst loading and reaction time at methanol-to-oil molar ratio 12:1 mol/mol resulted from the reduced quadratic model. It was obvious that the FAME content increased with the increase of both catalyst loading and reaction time. The influence of the catalyst amount on FAME content was

more significant at a shorter reaction time, while it decreased at a longer reaction time. Such a behavior could be attributed to approaching the reaction to the equilibrium when the FAME formation rate slowed down. The reaction time was more influential at lower catalyst amounts and became less significant at higher catalyst amounts, which was ascribed to the faster reaction rate at a higher catalyst amount because of the higher concentration of catalytically active sites, enabling the completion of the transesterification reaction rate for a shorter reaction time. The significant influence of catalyst amount and reaction time on FAME content was previously reported for the corn oil transesterification over a CaO-based catalyst obtained from snails' shells (El-Gendy et al., 2014) and the corn oil transesterification with dimethyl carbonate over solid KOH (Sun et al., 2014). According to Mustata and Bicu (2014), the catalyst amount had a significant influence, while the effect of the reaction time on the corn oil

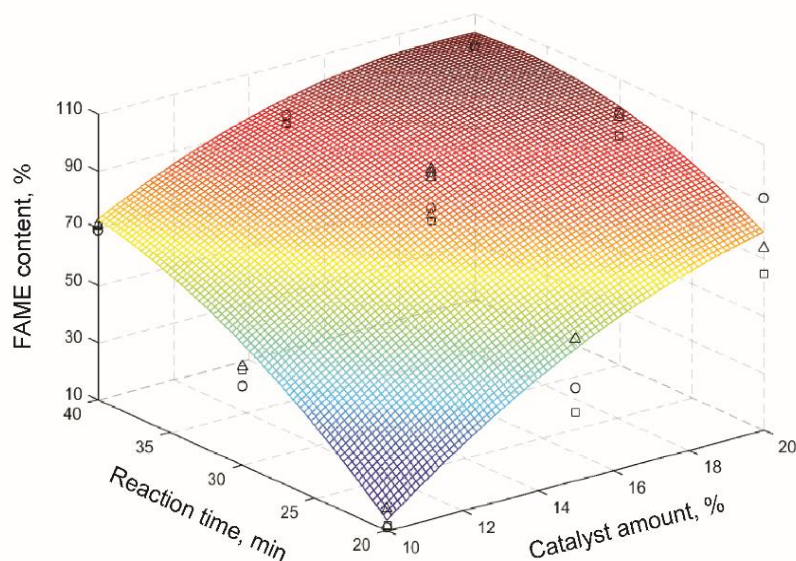


Figure 1. Response surface plot for FAME content as a function of catalyst loading and reaction time (surface corresponds to methanol-to-oil molar ratio of 12:1; actual FAME content at various methanol-to-oil molar ratios: 9:1 – ○, 12:1 – Δ and 15:1 – □)

conversion was insignificant in the presence of barium hydroxide as a catalyst and dimethyl ether as a cosolvent. Opposite to the present study, the methanol-to-oil ratio was designated in the previous studies as the process factor with a significant influence on the FAME conversion, which could be explained by the differences in the process conditions applied in different studies, such as the presence of cosolvents, the type of acyl acceptor and the range of the experimental conditions.

The optimum reaction conditions for achieving the highest FAME content were determined based on the reduced quadratic model. The FAME content above 98 % could be obtained at the catalyst amount over 15.3 %, the methanol-to-oil molar ratio in the range 9.3 - 14.2 mol/mol and the reaction time longer than 31 min. The optimum reaction conditions were selected as follows: the catalyst amounts of 19.8 %, the methanol-to-oil molar ratio of 9.4 mol/mol and the reaction time of 31 min, under which the predicted FAME content was 98.4 % that agreed well with the experimentally obtained value of 98.1 %.

4. Conclusion

Corn germs and corn cobs as byproducts from corn-based starch production were shown to be the suitable feedstocks for the biodiesel production by the methanolysis of the oil extracted from corn germs, which was catalyzed by the ash produced by combustion of corn cobs. The RSM and the ANOVA showed that only the catalyst amount, the reaction time, the catalyst amount interaction with reaction time and all three quadratic terms had a statistically significant influence on FAME content with the confidence level of 95 %. The optimum

reaction conditions were the catalyst amounts of 19.8 %, the methanol-to-oil molar ratio of 9.4 mol/mol and the reaction time of 31 min and provided the FAME content of 98.1 %, which was in an excellent agreement with the predicted FAME content (98.4 %).

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Optimizacija proizvodnje biodizela kukuruznog ulja metanolizom katalizovanom pepelom kurdeljke

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I Z V O D

Upotreba jeftinih ili bezvrednih sirovina, kao što su sporedni proizvodi, u proizvodnji biodizela ima za rezultat smanjene ukupne troškove procesa. U ovom radu su prikazani rezultati upotrebe kukuruznih klica i okrunjenog kukuruznog klipa (kurdeljke, krudeljke) kao sporednih proizvoda iz proizvodnje kukuruznog skroba u proizvodnji biodizela metanolizom ulja izdvojenog iz kukuruznih klica, katalizovane pepelom dobijenim sagorevanjem kurdeljke. Glavni cilj je bila optimizacija molskog odnosa metanol-ulje, količine katalizatora i reakcionog vremena u šaržnom reaktoru sa mešanjem u odnosu na sadržaj metilestra masnih kiselina (MEMK). Statističko modelovanje i optimizacija izvršeni su korišćenjem kvadratnog modela, razvijenog metodologijom odzivne površine, u kombinaciji sa 3³ faktorijelnim planom sa 3 centralne tačke. Sadržaj MEMK-a je određen metodom tečne hromatografije pod visokim pritiskom. Analiza varijanse je pokazala da su samo uticaji količine katalizatora, reakcionog vremena, interakcije količine katalizatora sa reakcionim vremenom i sva tri kvadratna člana statistički značajni sa nivoom pouzdanosti od 95 %. Pod optimalnim reakcionim uslovima (količina katalizatora 19,8 %, molski odnos metanol/ulje 9,4 mol/mol i reakciono vreme 31 min) dobijen je sadržaj MEMK-a od 98,1 %, koji se slaže sa predviđenim sadržajem MEMK-a (98,4 %). Prema tome, i kukuruzne klice i kurdeljka mogu biti pogodne sirovine za proizvodnju biodizela.