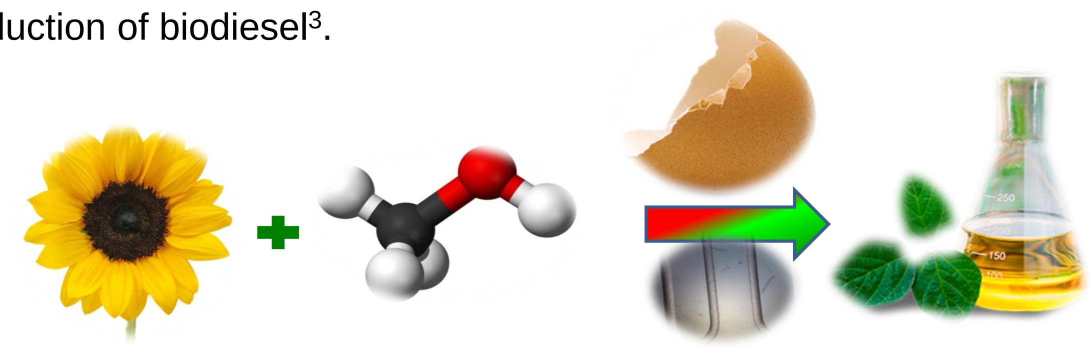
OPTIMIZATION OF HETEROGENEOUSLY CATALYZED METHANOLYSIS IN MICROREACTOR USING A GREEN EGGSHELL CATALYST

Stefan Pavlović, Dalibor Marinković, Marina Tišma, Miroslav Stanković

Chair Name

Introduction

- CaO-based catalysts are known as highly active, easily accessible and low price catalytic materials and are widely used for the transesterification of vegetable oils to biodiesel[2].
- A special place in the research is occupied by microreactors which achieve intensification in the production of biodiesel[3].



- In present study, the eggshell catalyzed methanolysis in microreactor was optimized. The eggshell catalyst was prepared by calcination and re-hydration involving calcination-hydration-dehydration-calcination steps[1].

Objective

Eggshell treatment
- calcination at 900 ºC, 4 h

Catalyst synthesis

Hydration-dehydration-calcination
- S:L = 1:5; 60 ºC, 6 h
- filtration and drying
- 600 ℃, 4 h

Methanolysis reaction

Microreactror system
- Optimization of reaction parameters (residence time, volume ratio, catalyst concentration)
- Methanolysis reaction was carried at 60 ℃

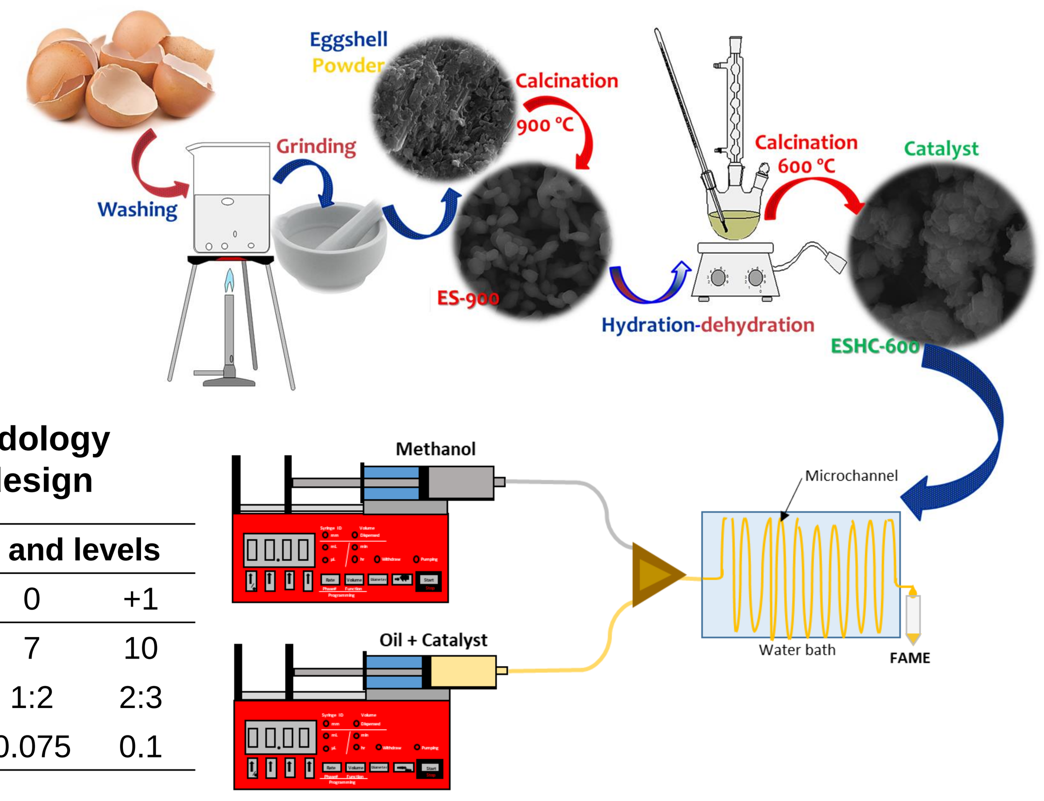
Targets

- ✓ Utilization of eggshell
- ✓ Development of microreactor system
- ✓ Eggshell catalyzed methanolysis in microreactor
- ✓ Optimization of process

Methodology

Catalyst synthesis and reaction setup

Microchannel with an internal diameter of **0.6 mm** was connected with syringes by T-shaped three-way junction and immersed in the thermostated water bath (60 °C).



Optimization of methanolysis

DoE method: **Responce surface methodology** combined with **Box-Behnken factorial design**

Factors	Symbol (unit)	Range and levels		
		-1	0	+1
Residence time	t (min)	4	7	10
MeOH/Oil voulme ratio	MR (v/v)	1:3	1:2	2:3
Catalyst concentration	C (g/g)	0.05	0.075	0.1

Results and discussions

Table 1. Experimental design for independent variables and response

Run	Manipulated variables			Response
	X_t	X_C	X_{MR}	FAME, %
1	7	0.1	3	28.48
2	4	0.075	3	9.14
3	7	0.05	3	8.91
4	7	0.1	1.5	30.57
5	10	0.05	2	9.04
6	10	0.1	2	51.12
7	7	0.05	1.5	4.81
8	10	0.075	3	32.02
9	7	0.075	2	6.43
10	7	0.075	2	7.63
11	4	0.1	2	13.62
12	4	0.05	2	0.28
13	4	0.075	1.5	2.08
14	10	0.075	1.5	18.51
15	7	0.075	2	8.36

- Experimental design and results of tests are presented in Table 1.
- Quadratic model for FAME content was obtained and presented in the follow equation:

$$FAME = 102.84 - 11.68 \cdot X_t - 1636.75 \cdot X_C - 25.63 \cdot X_{MR} + 95.80 \cdot X_t \cdot X_C + 0.72 \cdot X_t \cdot X_{MR} - 82.53 \cdot X_C \cdot X_{MR} + 0.46 \cdot X_t^2 + 11037.33 \cdot X_C^2 + 6.79 \cdot X_{MR}^2$$

- The experimental obtained values and predicted values by quadratic model for FAME content were presented in Figure 1.

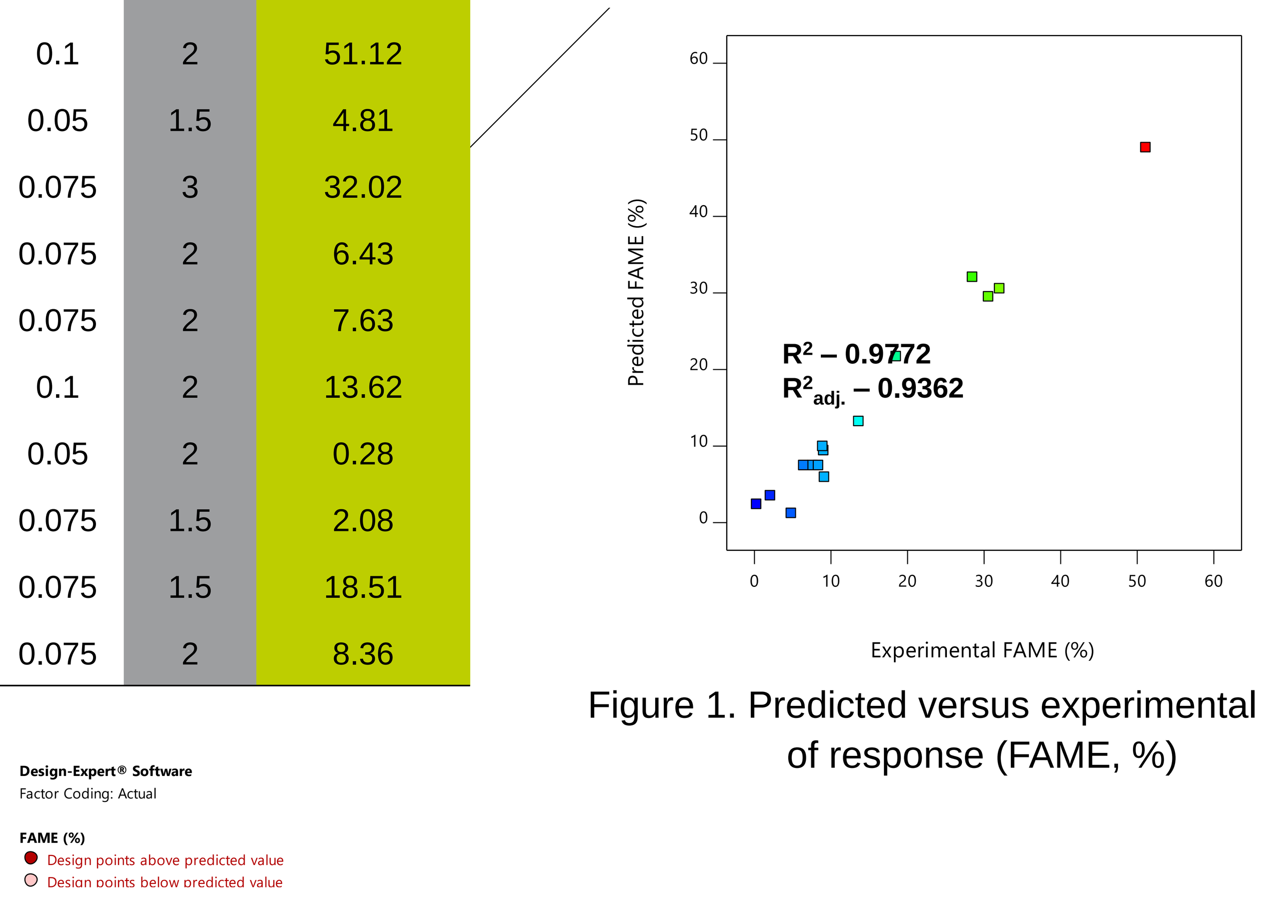


Figure 1. Predicted versus experimental values of response (FAME, %)

ANOVA analysis

- The $\mathbf{R^2}$ and $\mathbf{R^2_{adj.}}$ of FAME content model were **0.977** and **0.936**, respectively.
- **F-value** calculated was **23.83** and implies that model is significant.
- **P-values** less than 0.0500 indicate model terms are significant. In present model **A, B, AB, B²** are **significant** model terms.
- The *Lack of Fit* F-value of 21.70 implies the ***Lack of Fit*** **is significant**.

- The surfaces and contours (Figure 3a-c) show relationship between the variables during their interaction.
- The methanolysis conditions were optimized to achieve high FAME content.
- The maximum **FAME content** of **51.12%** was achieved in a **residence time** of **10 min**, **catalyst concentration** of **0.1 g/g**, and **methanol to oil volume ratio** of **1:2**.
- It can be seen that FAME content increases with residence time and catalyst concentration increase.

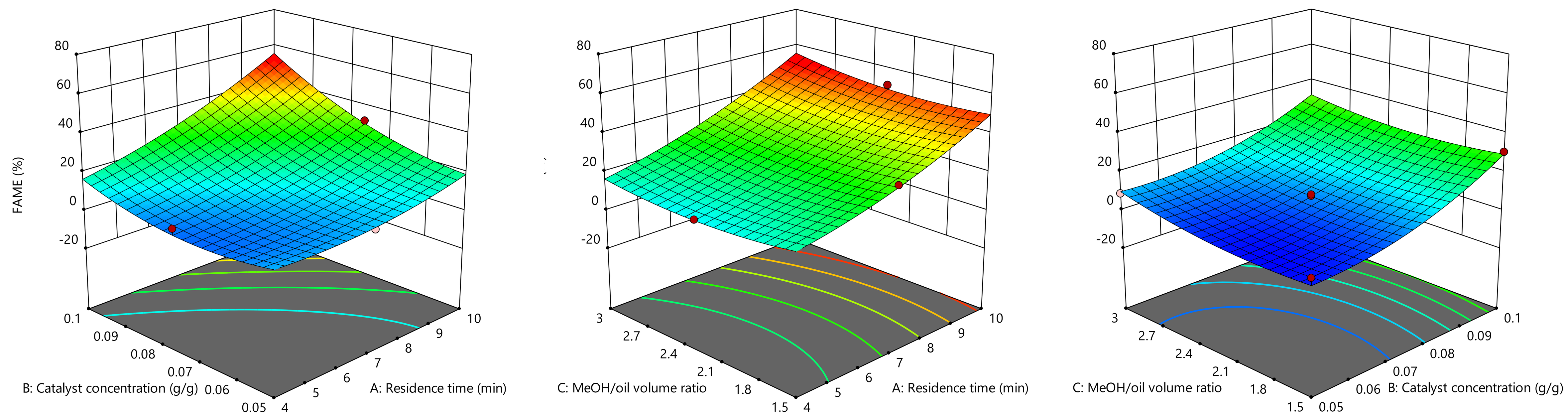


Figure 2. Response surface (3D) plots for the (a) catalyst concentration and residence time interaction (b) methanol to oil volume ratio and residence time interaction and (c) methanol to oil volume ratio and catalyst concentration interaction

Conclusions

- ✓ The catalyst exhibits satisfactory catalytic activity in microreactor systems in which two immiscible liquids and a solid catalyst interact at a micro-level.
- ✓ Determined **optimal reaction conditions** were: **catalyst concentration** of **10 wt%, methanol to oil volume ratio** of **2:1**, and **residence time** of **10 min**.
- ✓ FAME content in microreactor (54.8 % FAME) was 5 times higher compared with the reaction in a batch reactor (10.3 % FAME) under optimal conditions.
- ✓ It is important to note that potential problem in such microreaction systems represents catalyst precipitation in the syringe, which is particularly pronounced at longer residence time.
- ✓ According to obtained results, such designed reaction systems can be used in the biodiesel production in large scale using sustainable, green and energy efficient processes, whereby productivity would be increased by connecting more of these reactors in series.

References

[1] S.M.Pavlović, D.M. Marinković, M.D.Kostić, I.M.Janković-Častvan, Lj.V.Mojović, M.V.Stanković, V.B.Veljković, Fuel, **2020**, 267, 1171171

[2] D.M. Marinković, M.V. Stanković, A.V. Veličković, J.M. Avramović, M.R. Miladinović, O.O.Stamenković, V.B. Veljković, D.M. Jovanović, Renew. Sust. Energ. Rev. **2016**, 56, 1387-1408

[3] N.N.Tran, M.Tišma, S. Budžaki, E.J.McMurchie, O.M.Morales Gonzales, V.Hessel, Y.Ngothai, Appl. Energy, **2018**, 229, 142-150