Purification of biodiesel produced by lipase catalysed transesterification by two-phase systems based on deep eutectic solvents in a microextractor: Selection of solvents and process optimization

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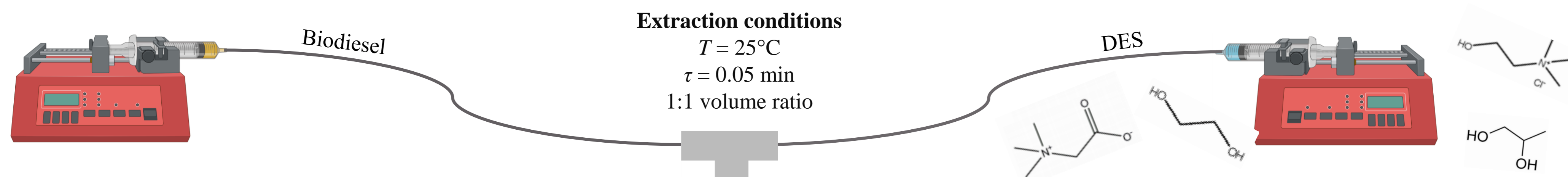
INTRODUCTION

Biodiesel is an **alternative diesel fuel** which is made from renewable biological sources. Biodiesel **produced by transesterification** is not suitable for application in engines since it contains soap (if biodiesel is produced by chemical catalysis), traces of the catalyst, methanol, metals, water, oil, and glycerides. **Priority for** biodiesel **industry is to** find solution to **remove** those **impurities,** especially glycerol [1]. The most dominant industrial method for the biodiesel purification is wet washing, which generates up to 10 L of wastewater per 1 L of purified biodiesel. **Deep eutectic solvents (DESs)** have been already demonstrated as **viable option in** biodiesel **purification**, because they are considered less toxic to the environment, non-volatile, biodegradable and more stable. In other words, they are economically and environmentally friendly in comparison with organic solvents [2].

Extraction conditions
T = 25°C
τ = 0.05 min
1:1 volume ratio

Biodiesel

DES

d = 1000 μm
L = 30 cm

analysis

Gas chromatography

TWO-PHASE LIQUID EXTRACTION IN A MICROEXTRACTOR

A two-port microextractor (length 30 cm, diameter 1000 μm) was used for the extraction process. One input stream contained biodiesel and the other input stream contained DES. The flow rates of biodiesel and DES were adjusted to obtain desired ratios of both inputs, meaning that values were changed from φ = 5 to 5000 μL/min. The experiments were performed at temperatures of 25°C, 40°C and 55°C.
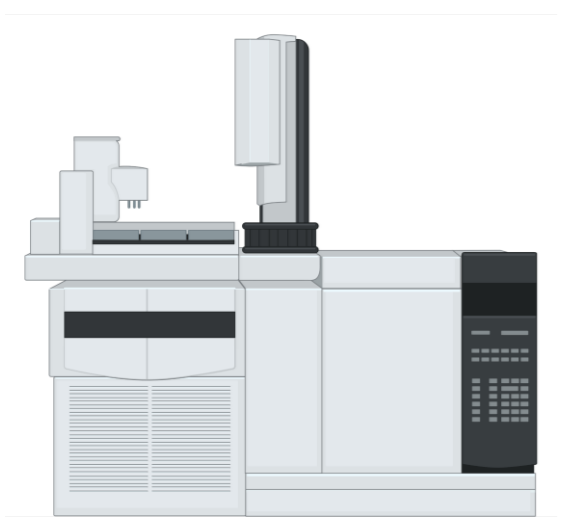
MATERIALS AND METHODS

In this study, **13 different DESs were synthesized and characterized** and then used for glycerol extraction in biodiesel purification process. Fast screening was performed under same initial conditions and three **DESs** which showed the best extraction efficiency **were used for process optimization**. A three-level-three-factor Box-Behnken optimization method was applied in order to obtain optimal process condition meaning best volume ratio of biodiesel to DES, process temperature and residence time for glycerol extraction. Gas chromatography (Shimadzu GC-2014) was used to determine the concentration of glycerol before and after extraction in biodiesel.

RESULTS AND DISCUSSION

Phase I - As it can be seen in Figure 1., the best results were observed for three DESs: choline chloride:glycerol (ChCl-Gly (1:3)), betaine-propylene glycol (B-PG) and choline chloride-ethylene glycol (ChCl-EG (1:3)) with extraction efficiency higher then 60%.
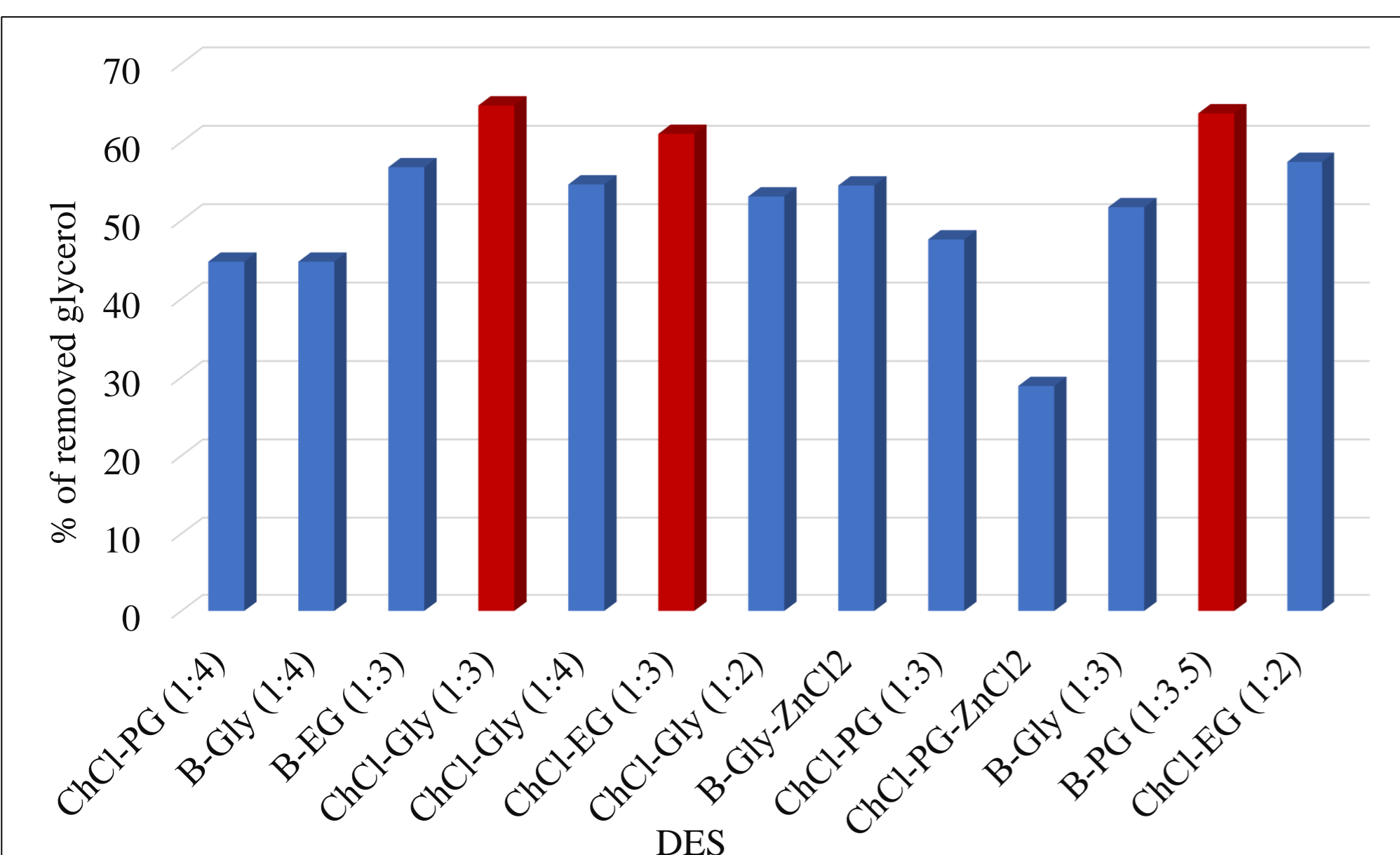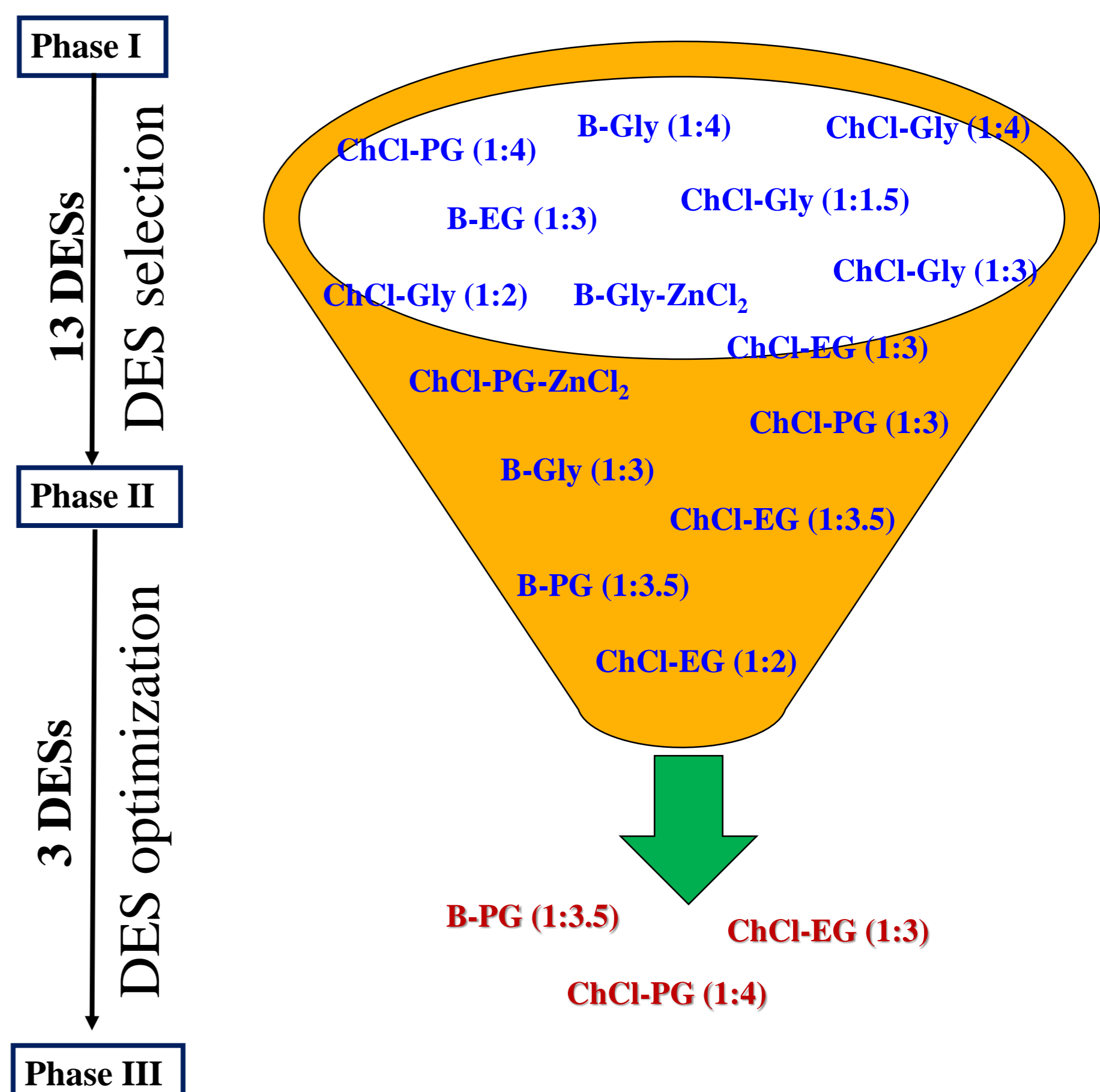

Figure 1. Percentage of removed glycerol from biodiesel using different DESs

Phase I — 13 DESs — DES selection

ChCl-PG (1:4)   B-Gly (1:4)   ChCl-Gly (1:4)
B-EG (1:3)   ChCl-Gly (1:1.5)
ChCl-Gly (1:2)   B-Gly-ZnCl₂   ChCl-Gly (1:3)
ChCl-PG-ZnCl₂   ChCl-EG (1:3)
B-Gly (1:3)   ChCl-PG (1:3)
B-PG (1:3.5)   ChCl-EG (1:3.5)
ChCl-EG (1:2)

Phase II — 3 DESs — DES optimization

B-PG (1:3.5)   ChCl-EG (1:3)   ChCl-PG (1:4)

Phase III

Phase II –According to the three-level-three-factor Box-Behnken experimental design total of 3x15 experiments plan was created in order to test three independent variables of the extraction efficiency of glycerol and fatty acid methyl esters (FAME) since it was noticed in previous phase that DESs extracts both components. All experiments were performed in a microextractor and the optimal process conditions under which minimum FAME and maximum of glycerol is extracted are presented in Figure 2.
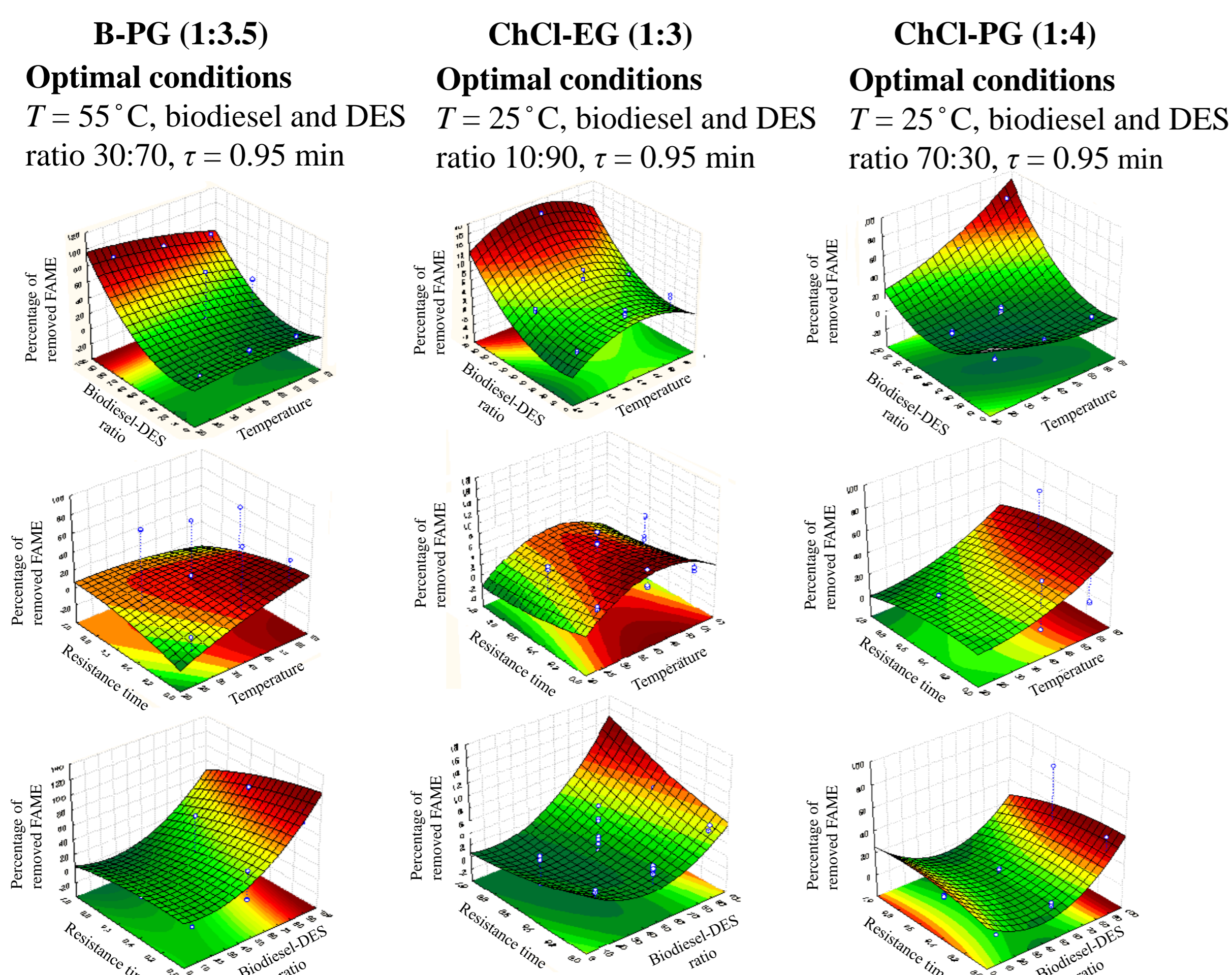
B-PG (1:3.5)
Optimal conditions
T = 55°C, biodiesel and DES ratio 30:70, τ = 0.95 min

ChCl-EG (1:3)
Optimal conditions
T = 25°C, biodiesel and DES ratio 10:90, τ = 0.95 min

ChCl-PG (1:4)
Optimal conditions
T = 25°C, biodiesel and DES ratio 70:30, τ = 0.95 min

Figure 2. Box-Behnken optimization – Fitted surface with variables: temperature, biodiesel-DES ratio, percentage of removed FAME and resistance time

Unfortunately, it has been observed that if the efficiency of glycerol extraction increases, efficiency of FAME extraction increases to and it was not possible to find a balance of process conditions under which glycerol would be removed and FAME retained in biodiesel. Based on the obtained results, it can be concluded that although DESs show potential in glycerol extraction, additional research must be conducted in order to selectively remove glycerol and retain esters in biodiesel, in an amount that defines the quality of biodiesel.

FURTHER WORK
Future work will be based on finding other DESs that will possess the property of selective extraction.

REFERENCES:
[1] Bewley, B. R., Berkaliev, A., Henriksen, H., Ball, D. B., & Ott, L. S. (2015), *Fuel Processing Technology*, 138, 419–423
[2] M. Cvjetko Bubalo, M. Panić, K. Radošević, I. Radojčić Redovniković, Croatian Journal of Food Technology, Biotechnology and Nutrition 11 (3-4), (2016) 164-168