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COSMO-RS-based Screening of Organic Solvents for Efficient Extraction of Rubber Seed Oil: Computational Prediction and Experimental Verification

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Predicting the interactions between solvent and solute molecules is one of the most prominent methods for the evaluation of separation performance. The infinite dilution activity coefficient and σ-profile, as a superior thermophysical properties, indicate the solubility of a solute and reflecting the strength of the interaction between solution's molecules. Depending on the infinite dilution activity coefficient of linoleic acid, as a representative for rubber seed oil, Conductor like Screening Model for Real Solvent (COSMO-RS) based screening was employed to select the efficient organic solvent for rubber seed oil extraction. The σ-profiles of linoleic acid and organic solvents were investigated for a better understanding of their similarity and interactions with solute. The experimental extraction of rubber seed oil was conducted in sono-reactor to validate the computational predictions. Based on the COSMO-RS prediction and experimental validation, diethyl ether and tetrahydrofuran exhibited the greatest capacity of 18.6 and 9.0 toward the solubility of linoleic acid and the highest experimental oil yields of 27.3 % and 27.0 % as well. Whereas, acetonitrile with capacity of zero revealed poor extraction efficiency of 7 (w/w)%. In conclusions general, the COSMO-RS method proves to be a helpful tool for estimating seed oil's solubility in organic solvents, allowing for the early diagnosis of the most efficient solvent

1. Introduction

Rubber tree is the key source of the milky latex which is the main source of natural rubber. Rubber tree is one of the fast-growing perennial plants distributed throughout Southeast Asia (Gunun et al., 2022). According to agricultural statistics from Malaysia Ministry of Plantation Industries & Commodities (MPIC)'s for 2020, rubber crop is the second major plantations following oil palm with a total area of 1.09 x 10^6 hectares (Mha) spread across 13 states (MPIC, 2021). In addition to latex, rubber trees also generate rubber seeds which are usually discarded as agricultural waste (Zhang et al., 2022). Rubber seed kernel contains up to 35-60% by weight of non-edible oils, which are high in unsaturated fatty acids (77-82%), primarily linoleic, linolenic, and oleic acids (Jisieike and Betiku, 2020). As part of the ongoing search for sustainable and inexpensive sources for biofuel production, oil from rubber seed are receiving increasing attention as a potential non-edible raw material for the manufacture of biodiesel (Tarigan et al., 2022). Rubber seed oil has also promising applications in a variety of industrial fields, including lubricants, paints and coatings, linseed oil replacement in paint and varnish, and toner cartridges (Jisieike and Betiku, 2020).

The common core methods for oil extraction from organic resources are solvent extraction, and enzymatic, mechanical extraction (Pikula et al., 2020). Solvent extraction techniques are the most frequently used technologies generating high yields of oil (Jisieike and Betiku, 2020). The efficiency of these techniques depends on the process parameters. Many studies evaluated the effect of different parameters on oil yield including extraction time, solid-solvent weight ratio and moisture content (Boonnoun et al., 2019). However, the nature of solvent and solute and their thermodynamic properties plays a crucial role for specific-task solvent selection. To

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the best of the authors' knowledge, none has investigated the impact of thermodynamic parameters, such as activity coefficient and surface interactions of species in fluid mixtures. One of the most promising and fast tools for solvent selection through predicting the thermodynamic properties of liquid solution's components is the Conductor-like Screening Model for Real Solvents (COSMO-RS) (Cheng et al., 2018). This model can be applied to evaluate the thermodynamic behavior of an single component and its affinity towards other component(s) in a mixture without requiring experimental data (Salleh et al., 2017). Panić et al., (2021) have applied COSMO-RS to screen deep eutectic solvents for the bioactive compounds' extraction from Graševina Grape Pomace. They confirmed that COSMO-RS was an efficient tool for selection of DES for polyphenols extraction by evaluating the activity coefficient.
Using COSMO-RS tool, this study for the first time investigates the role of thermodynamic parameters, including activity coefficient and surface interactions, in the prediction of 18 organic solvents' efficiency for the extraction of rubber seed oil. Considering that rubber seed oil comprises saturated fatty acids, linoleic acid was selected as model compound for rubber seed oil in the COSMO-RS screening (Hayyan et al., 2022). As an effective screening criterion, the infinite dilution activity coefficients, σ- profiles and the capacity of organic solvents for linoleic acid were evaluated. Through σ- profiles, the effect of surface segments nature on solubility performance of organic solvents was interpreted. Experimentally, extraction of rubber seed oil was conducted in sono-reactor to validate the COSMO-RS computational predictions.

2. Method

2.1 COSMO-RS screening

COSMO-RS is a time-saving and accurate technique for predicting the thermodynamic chemical characteristics of liquid mixtures without the necessity for experimental data (Hizaddin et al., 2014). Using TmoleX version 4.0 software with and the singlet default spin 6-31G basis set, the geometry of all compounds was optimized by employing the density functional theory (DFT) method (Alioui et al., 2020). A single-point density-functional-theory (DFT) calculation was performed at Becke Perdew 86 (BP86) using the Triple-Zeta Valence Potential (TZVPD) to generate the cosmo files (Hadj-Kali et al., 2017). Once complete, the .cosmo files were transferred to COSMOthermX version 19.0.5 using the BP_TZVPD_FINE_19.ctd parameterization (Wang et al., 2021).
The activity coefficient was determined using Eq (1) and Eq (2):

$$\ln(\gamma_i) = \frac{\mu_i^s - \mu_i^i}{RT} \tag{1}$$

$$\gamma_i^\infty = lim_{xi \to 0 \gamma i} \tag{2}$$

where the infinite dilution activity coefficient γ_i^∞ is described as the value of the activity coefficient $\gamma_i$as the concentration of solute i comes close to zero, μ_i^s is the chemical potential of the solvent S and μ_i^i is the chemical potential of the pure compound (Ozturk and Gonzalez-Miquel, 2019).
The solubility capacity $C_i^\infty$of organic solvents was calculated using Eq (3) to determine the maximum amount of linoleic acid that can be dissolved in the solvents:

$$C_i^\infty = 1/\gamma_i^\infty \tag{3}$$

2.2 Experimental RSO extraction

2.2.1 Chemicals and materials

Rubber seeds were collected from a local market and were ground and stored at room temperature for. Tetrahydrofuran, diethyl ether, ethyl acetate, 1-butanol, 1-propanol, acetone, isopropanol, dichloromethane, benzene, toluene, pentane, n-hexane and octane were procured from R&M Chemicals, UK. n-heptane, methanol, acetonitrile and ethanol were obtained from Merck (Darmstadt, Germany).

2.2.2 Ultrasonic assisted extraction

Initially, the rubber seeds were dried at 100 ˚C for 24 h, ground and stored at tightened flask until further use. The extraction process was done using sono-reactor. Accurately 3 g of grounded rubber seeds weighed and added to 6 g of organic solvent in a 50 mL clear glass laboratory bottle. The mixture was extracted by an ultrasonic irradiation for 60 min. Separation of the oil and solvents from oilseeds was carried out using centrifuge at a speed of 3500 rpm for 10 min. The solvent was removed from the extracted oil using a rotary evaporator at 70 °C. Finally, the oil yield was quantified according to Eq (4):

$$Y_{oil}\ (\%) = \frac{W_{oil}}{W_{seed}} \times 100\ \% \quad (4)$$

Where Y_{oil} is the oil yield, W_{oil} is the weight of oil extracted and W_{seed} is the weight of seed.

3. Results and discussion

3.1 Computational COSMO-RS predictions

3.1.1 Solubility prediction

The solubility of Linoleic acid was made based on its logarithmic activity coefficient at infinite dilution ($\ln \gamma^{\infty}$) according to the COSMO-RS method. The activity coefficient of linoleic acid in each of solvents was predicted at 30 °C and 100 kPa. The findings are given in Table 1. Typically, the activity coefficient values are expressed as $\ln \gamma$. The lower values of logarithmic activity coefficients reveal greater solubility of linoleic acid in the solvent (Słupek et al., 2020).

Table 1: Predicted logarithmic infinite dilution activity coefficients of linoleic acid in organic solvents

No.	Organic solvent	Polarity	ln(γ∞)
1	Tetrahydrofuran	Moderately Polar	-2.93
2	Diethyl ether	Moderately Polar	-2.20
3	Ethyl acetate	Moderately Polar	-0.82
4	Hexanol	Polar	-0.45
5	1-butanol	Polar	-0.15
6	1-propanol	Polar	0.12
7	Acetone	Moderately Polar	0.20
8	Isopropanol	Polar	0.21
9	Dichloromethane	Moderately Polar	0.57
10	Ethanol	Polar	0.75
11	Benzene	Non-polar	0.86
12	Toluene	Non-polar	1.25
13	Methanol	Polar	2.20
14	Pentane	Non-polar	2.85
15	n-Hexane	Non-polar	2.95
16	Acetonitrile	Polar	3.00
17	Heptane	Non-polar	3.03
18	n-Octane	Non-polar	3.09

A total of 18 organic solvents were screened using the COSMO-RS methodology. The smaller value of $\ln \gamma^{\infty}$ indicating the better affinity of towards the solvents (Hadj-Kali et al., 2017). As shown in Table 1, most of solvents (tetrahydrofuran, diethyl ether, ethyl acetate, hexanol, 1-butanol, 1-propanol, acetone and isopropanol) have small values of linoleic acid $\ln \gamma^{\infty}$, indicating a greater affinity of linoleic acid with these solvents. Whereas dichloromethane, ethanol, benzene, toluene, and methanol have moderate values of $\ln \gamma^{\infty}$. On the other hand, pentane, n-hexane, acetonitrile, heptane, and octane have the highest values of $\ln \gamma^{\infty}$ of linoleic acid, which indicates that linoleic acid has a low affinity toward such solvents. However, to evaluate the overall efficiency of solvents, the solubility's capacity for each solvent was calculated. As shown in Figure 1, tetrahydrofuran and diethyl ether have the highest solubility's capacities of Linoleic acid, which are 18.6 and 9. In contrast, pentane, n-hexane, acetonitrile, heptane and octane exhibit the lowest capacities close to zero.

3.1.2 σ-profile analysis

The extraction performance of solvents is deduced from molecules' interactions with the help of their σ-profiles. To evaluate the interactions between solvents and extractant molecules, σ-profiles of organic solvents and linoleic acid were interpreted. Through the probability distribution of surface area with charge density (of all segments of molecular surfaces), COSMO-RS may calculate the σ-profile which is an important molecular thermodynamic property interprets the interaction between compounds and their molecular constituents. (Lemaoui et al., 2020). Positive sigma-profile values correspond to negative polarity, whereas negative sigma-profile values correspond to positive polarity (Benabid et al., 2019). σ-profile is typically distributed into three regions, namely the hydrogen bond donor (HBD) region (σ < -0.0082 e/Å^2), the non-polar region (-0.0082 e/Å^2 < σ < 0.0082 e/Å^2) and the hydrogen bond acceptor (HBA) region (σ > 0.0082 e/Å^2) (Qin et al., 2022). Usually, the higher similarity of σ-profile between the solvents and linoleic acid molecules during the nonpolar region and

opposite equivalent parts through the polar regions, the better the interaction as well as solubility of linoleic acid in solvents (Wang et al., 2021).

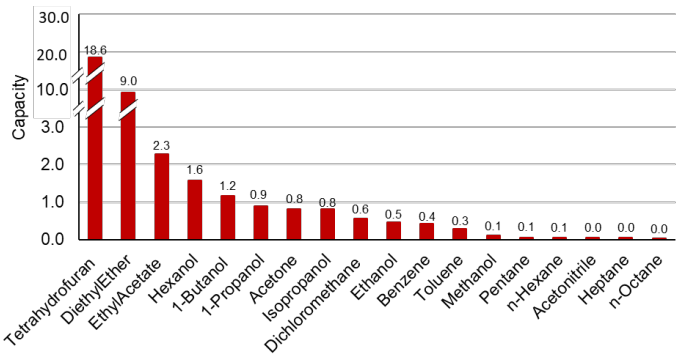

Figure 1: predicted solubility capacity of organic solvents for linoleic acid at infinite dilution

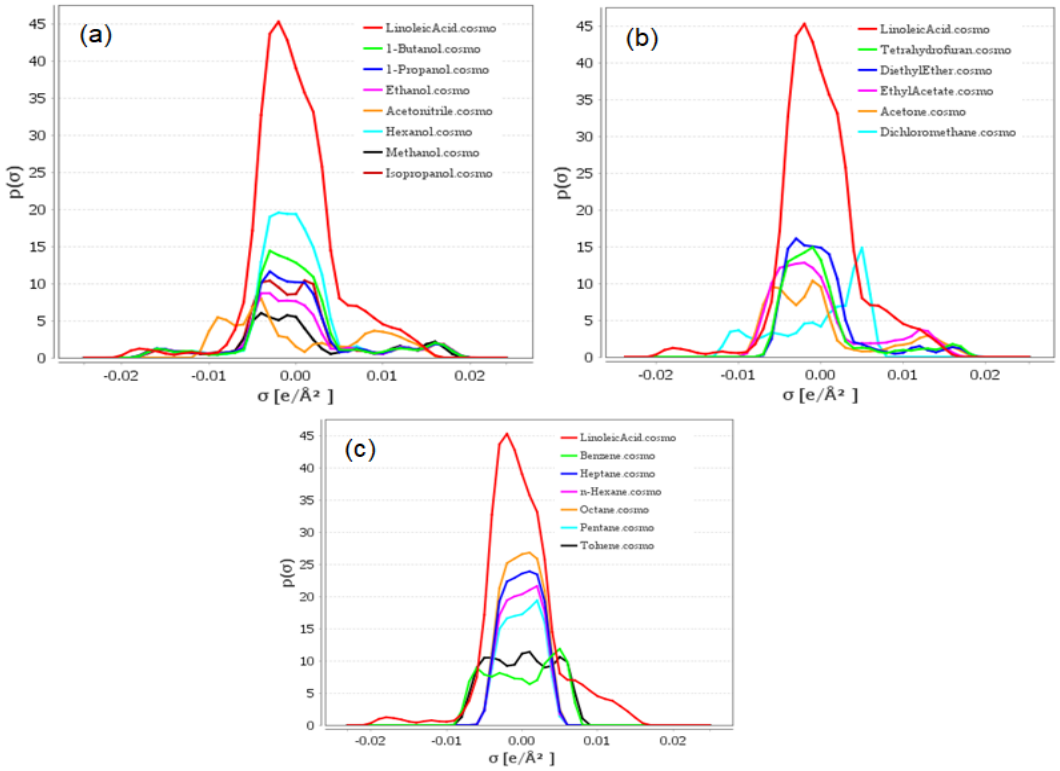

Figure 2: σ-profile of linoleic acid and organic solvents: (a) polar solvents, (b) moderately polar solvents, and (c) non-polar solvents

Figures 2(a), 2(b) and 2(c) compare σ-profiles of linoleic acid and used polar, moderately polar and non-polar organic solvents. The symmetric peak of linoleic acid is located primarily in the nonpolar zone in a range of -0.0084 e/Å^2 < σ < 0.005 e/Å^2 with a center around 0.001, it has a minor peak positioned at HBD region of σ = -0.018 e/Å^2 related to the H atoms in the linoleic acid structure, and it also has small part extended to HBA region up to σ = 0.015 e/Å^2 due to the O atoms. Subsequently, to achieve a higher interaction with linoleic acid molecules, it is better for solvents to be nonpolar species with a small peak located at HBA region or small one located at HBD (Benabid et al., 2019).

For polar solvents, Figure 2(a) demonstrates that profile of each of hexanol, 1-butanol, 1-propanol, isopropanol, ethanol and methanol has a moderate affinity to linoleic acid with a narrow peak in the nonpolar area. However, each of these alcohols exhibit another and two small peaks, one at each of HBA and HBD area, which enables some interactions between their molecules in the polar regions rather than interactions with acid molecules.

With completely different σ-profile, acetonitrile has a broad peak exhibiting less affinity to linoleic acid surface segment. Therefore, its strong polar nature suggesting very weak interactions with linoleic acid molecules.
Figure 2(b) compares the σ-profiles of moderately polar solvents with linoleic acid profile. Each of tetrahydrofuran, diethyl ether and ethyl acetate exhibit closer surface segments nature to linoleic acid. Their σ-profile consist of narrow peak in the nonpolar region, in addition to a small peak at HBD region. Slightly different, profile acetone reveals that it has nonpolar peak has two small peaks which enable some interactions between the molecules of solvent itself in the nonpolar region. On the other hand, with a broad peak, dichloromethane significantly deviate from the linoleic acid profile suggesting weak interaction between their molecules. In general, surface segments nature of all moderately polar solvents, except dichloromethane, reveal that there is a great chance to their molecules to interact with linoleic acid molecules, since they have big peaks at nonpolar region and small peaks at HBD region.
Finally, Figure 2(c) displays the σ-profiles of nonpolar solvents. Pentane, n-hexane, heptane and octane are narrowly allocated in the nonpolar region around zero (Zurob et al., 2020). Since they are strong nonpolar compounds, their molecules have good chances to interact with linoleic molecules. Similarly, benzene and toluene distributed in the nonpolar region. However, they have broad peaks consisting of three small peaks, indicating limited molecules interactions with acid.

3.2 Experimental validation of RSO extraction

Comparing to the computational solubility performance of organic solvents, the experimental extraction efficiency of solvents for extraction of RSO generally agree reasonably with the predicted sequence of activity coefficient and σ-profile analysis. Medium polarity solvents (tetrahydrofuran and diethyl ether) gave the highest RSO yields, which gave 27.33 % and 27 %. These results agree well with their predicted activity coefficients and σ-profile analysis as well. In contrast, acetonitrile generates the lowest RSO yield of 13.2 %, which similarly agrees with its infinite dilution activity coefficients and σ-profile. On the other hand, pentane, n-hexane, heptane and octane exhibited extraction efficiencies better than those solvents with moderate activity coefficients. This is attributed to non-polarized nature of these compound as seen in their σ-profile, which enhance their interactions with nonpolar part of linoleic acid as representative for RSO.

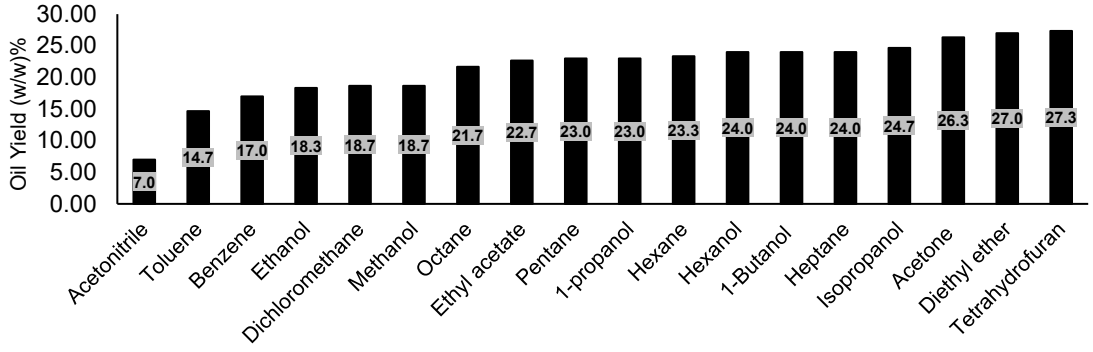

Figure 3: Effect of organic solvent type on the oil yield

4. Conclusions

The extraction performance of 18 organic solvents for rubber seed oil were evaluated using COSMO-RS model and validated experimentally in sono-reactor to validate the computational predictions. The activity coefficient at infinite dilution and σ-profile were analyzed to evaluate the potential solubility and interactions between solution's molecules. The results revealed that the surface segment nature has significant impacts on the extraction performance. Tetrahydrofuran and diethyl ether as closer surface segments nature to linoleic acid were the most promising and efficient medium for oil extraction, generating oil yields of 27.3 % and 27.0 %. In contrast, acetonitrile was the less surface affinity for linoleic acid, reflecting in its poor extraction efficiency of 7 (w/w)%. It could be concluded that COSMO-RS technique proves to be a useful tool for predicting the solubility of rubber seed oil in organic solvents, thus making it possible to screen for the most effective solvent.

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References

Alioui O., Benguerba Y., and Alnashef I.M., 2020, Investigation of the CO_2-solubility in deep eutectic solvents using COSMO-RS and molecular dynamics methods, Journal of Molecular Liquids, 307, 113005.

Benabid S., Benguerba Y., AlNashef I.M., and Haddaoui N., 2019, Theoretical study of physicochemical properties of selected ammonium salt-based deep eutectic solvents, Journal of Molecular Liquids, 285, 38–46.

Cheng H., Liu C., Zhang J., Chen L., Zhang B., andQi, Z., 2018, Screening deep eutectic solvents for extractive desulfurization of fuel based on COSMO-RS model, Chemical Engineering and Processing: Process Intensification, 125, 246–252.

Gunun N., Ouppamong T., Khejornsart P., Cherdthong A., Wanapat M., Polyorach S., Kaewpila C., Kang S., Gunun P., 2022, Effects of rubber seed kernel fermented with yeast on feed utilization, rumen fermentation and microbial protein synthesis in dairy heifers, Fermentation, 8(6), 1–10.

Hadj-Kali M.K., Hizaddin H.F., Wazeer I., El blidi L., Mulyono S., Hashim M.A., 2017, Liquid-liquid separation of azeotropic mixtures of ethanol/alkanes using deep eutectic solvents: COSMO-RS prediction and experimental validation, Fluid Phase Equilibria, 448, 105–115.

Hayyan A., Samyudia A.V., Hashim M.A., Hizaddin H.F., Ali E., Hadj-Kali M.K., Aldeehani A.K., Alkandari K.H., Etigany H.T., Alajmi F.D., Alhumaydhi F.A., Aljohani A.S.M., Zulkifli M.Y., Halilu A., Yeow A.T.H., 2022, Application of deep eutectic solvent as novel co-solvent for oil extraction from flaxseed using sonoenergy, Industrial Crops and Products, 176, 114242.

Hizaddin H.F., Ramalingam A., Hashim M.A., Hadj-Kali M.K.O., 2014, Evaluating the performance of deep eutectic solvents for use in extractive denitrification of liquid fuels by the conductor-like screening model for real solvents, Journal of Chemical and Engineering Data, 59(11), 3470–3487.

Jisieike C.F., Betiku, E., 2020, Rubber seed oil extraction: Effects of solvent polarity, extraction time and solid-solvent ratio on its yield and quality, Biocatalysis and Agricultural Biotechnology, 24, 101522.

Lemaoui T., Darwish A.S., Hammoudi N.E.H., Abu Hatab F., Attoui A., Alnashef I.M., Benguerba Y., 2020, Prediction of electrical conductivity of deep eutectic solvents using COSMO-RS sigma profiles as molecular descriptors: A quantitative structure-property relationship study, Industrial and Engineering Chemistry Research, 59(29), 13343–13354.

Malaysia Ministry of Plantation and Commodities (MPIC), 2021, http://www.kppk.gov.my/, Accessed 15 September 2022

Ozturk B., Gonzalez-Miquel M., 2019, Alkanediol-based deep eutectic solvents for isolation of terpenoids from citrus essential oil: Experimental evaluation and COSMO-RS studies, Separation and Purification Technology, 227), 115707.

Panić M., Gunjević V., Radošević K., Bubalo M.C., Ganić K.K., Redovniković I.R., 2021, Cosmotherm as an effective tool for selection of deep eutectic solvents based ready-to-use extracts from Graševina grape pomace, Molecules, 26(16).

Pikula K., Zakharenko A., Stratidakis A., Razgonova M., Nosyrev A., Mezhuev Y., Tsatsakis A., Golokhvast K., 2020, The advances and limitations in biodiesel production: feedstocks, oil extraction methods, production, and environmental life cycle assessment, Green Chemistry Letters and Reviews, 13(4), 11–30.

Qin Z., Cheng H., Song Z., Ji L., Chen L., Qi Z., 2022, Selection of deep eutectic solvents for extractive deterpenation of lemon essential oil, Journal of Molecular Liquids, 350, 118524.

Quaid T., Reza M.T., 2021, Carbon capture from biogas by deep eutectic solvents: A COSMO study to evaluate the effect of impurities on solubility and selectivity, Clean Technologies, 3(2), 490–502.

Salleh Z., Wazeer I., Mulyono S., El-blidi L., Hashim M.A., Hadj-Kali M.K., 2017, Efficient removal of benzene from cyclohexane-benzene mixtures using deep eutectic solvents – COSMO-RS screening and experimental validation, Journal of Chemical Thermodynamics, 104, 33–44.

Słupek E., Makoś P., Gębicki J., 2020, Theoretical and economic evaluation of low-cost deep eutectic solvents for effective biogas upgrading to bio-methane, Energies, 13(13).

Tarigan J.B., Anggraini R., Sembiring R.P., Supeno M., Tarigan K., Ginting J., Karo-Karo J.A., Sitepu E.K., 2022, Waste rubber seeds as a renewable energy source: Direct biodiesel production using a controlled crushing device, RSC Advances, 12(4), 2094–2101.

Wang J., Guo Y., Liu F., Zhang X., Wang W., Peng Q., 2021, COSMO-RS prediction and experimental verification of deep eutectic solvents for water insoluble pesticides with high solubility, Journal of Molecular Liquids, 349, 118139.

Zhang X., Rong M., Cao H., Tan T., 2022, One-pot synthesis of rubber seed shell-derived N-doped ultramicroporous carbons for efficient CO_2 adsorption, Nanomaterials, 12(11).

Zurob, E., Cabezas, R., Villarroel, E., Rosas, N., Merlet, G., Quijada-Maldonado, E., Romero, J., Plaza, A. 2020. Design of natural deep eutectic solvents for the ultrasound-assisted extraction of hydroxytyrosol from olive leaves supported by COSMO-RS. Separation and Purification Technology, 248, 117054.