Conventional and ultrasound-assisted extraction of rice bran oil with isopropanol as solvent

S. Fraterrigo Garofalo[1], F. Demichelis[1], Giuseppe Mancini[2], T. Tommasi[1], D. Fino[1]

[1]Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca Degli Abruzzi 24 Torino, 10129, Italy
[2]Department of Electric, Electronic and Computer Engineering, University of Catania, Viale A. Doria 6, Catania 95125, Italy

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Presenting author email: silvia.fraterrigo@polito.it

Rice is one of the world's most important food crops. According to FAO, the annual global paddy rice production exceeds 700 million tons. After the cereal crops, rice is subjected to several milling processes to remove hull, germ, and bran and produce the final and edible white rice. Around 40% of the total grain is lost during the milling process in the form of by-products, and they are usually discarded or used for animal feeds.

The bran, an external layer of the rice grain, represents around 9% of total weight and is usually considered waste material. However, it is full of nutrients as proteins, dietary fibers, minerals, and lipids, including their unsaponifiable fraction rich in γ-oryzanol.

γ -oryzanol is a complex mixture of ferulic acid esters of phytosterols and triterpenoids, which has shown many health benefits, including antioxidant, anti-inflammatory, and anti-hypercholesterolemic properties. One of the most common rice bran applications is the extraction of rice bran oil (RBO) (Fraterrigo Garofalo *et al 2020*).

The conventional method for extracting RBO is solvent extraction through organic solvents (typically hexane), which are flammable, volatile, toxic for health and the environment (Garba e*t al* 2017). Due to these undesirable proprieties, researchers are focusing on alternative green extraction procedures exploiting non-conventional solvents or involving new technologies to intensify the process. Short-chain alcohols, mainly ethanol and isopropanol, have been proposed as alternative extraction solvents due to their greater safety and polarity.

One promising key-technology in reaching the purpose of more sustainable and green extraction is represented by ultrasound-assisted extraction (Chemat *et al* 2017). Ultrasound-assisted extraction is an environmentally friendly process that allows a reduction of the extraction time, with high reproducibility, and at the same time maintains the high-purity of the final product (Fraterrigo Garofalo *et al 2020*).

In this work, RBO was extracted through two non-conventional solvent extraction strategies: i) isopropanol as the non-conventional solvent and ii) isopropanol ultrasound-assisted extraction. These two green extraction techniques were compared concerning oil yield and γ-oryzanol content; moreover, their environmental impacts were evaluated through a Life Cycle Assessment analysis (LCA).

Isopropanol was chosen because it is an alcohol with polarity intermediate between water and hexane; it is recommended as a substitute for organic solvents by several green solvent selection guides (Fergal P. Byrne et al 2016). Moreover, many other studies show an excellent extraction capacity.

The RBO solvent extraction was performed in a round-bottomed reaction flask connected to a Liebig condenser under controlled temperature and stirring. The temperature was kept at 90 °C through a water bath, and rice bran to isopropanol ratio of 1/9 was used. The ultrasound-assisted extraction was performed using the same bran to isopropanol ratio, but at room temperature; the ultrasound was generated by an Ultrasonic probe-type system, Sonics VCX750. The γ-oryzanol content was determined by reverse-phase HPLC analysis. Both extraction techniques were compared to a conventional hexane extraction.

The RBO yield and the γ-oryzanol content were monitored over time. As shown in Figure 1, Peleg's model was used to evaluate the extraction kinetics.

The knee-point can be exploited to determine the best trade-off between productivity and process extent. Figure 1 highlights that the ultrasound-assisted extraction produces yield in RBO slightly lower than solvent extraction reaching the maximum at only 60 seconds, whereas the knee-point of isopropanol extraction is reached at 15 minutes. The analysis showed the same trend for the γ-oryzanol content. Both extractions showed higher yield in RBO and γ-oryzanol than using conventional hexane extraction. These data show that the substitution of hexane by isopropanol is technically feasible for the extraction of oil from rice bran. Moreover, the process intensification operated by ultrasound allows the completion of the full extraction in one minute with high reproducibility. The results suggest that the ultrasound-assisted extraction might be the best choice in terms of process sustainability since it allows operating at room temperature, significantly reducing the reaction times and obtaining time comparable quantities to conventional isopropanol extraction.

An LCA analysis was conducted to confirm this hypothesis and analyze and compare the environmental performances and the energy sustainability of these two laboratory-scale extraction techniques. For all extraction processes, the environmental profiles were dominated by the electricity use for heating and isopropanol's production and use as solvent; these two elements have generated the highest contribution in most of the impact categories.

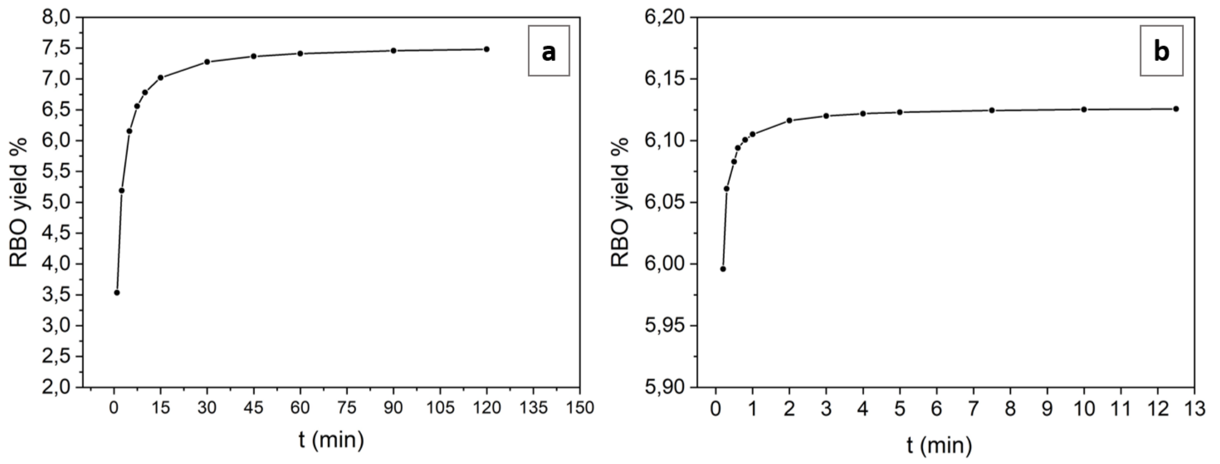

Figure 1. RBO extraction kinetics curves modelled by Peleg's equation. Curve "a" shows the yield obtained through solvent extraction, and curve "b" the yield obtained by ultrasound-assisted extraction.

Results show that, the ultrasound-assisted extraction is the best environmental sustainable process. These outcomes highlight the importance of evaluating a process from an environmental point of view to be fully in line with the principles of green chemistry and circular economy.

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