# Supercritical Extraction of Oil Seed Rape: Energetic Evaluation of Process Scale

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## ABSTRACT

This study focuses upon the supercritical $CO_2$ extraction of rape seed oil and the energy consumption associated with it in two different scales. Several experiments were carried out to determine the influence of pressure, temperature and flow rate on the extraction yield. Small scale extraction trials were carried out using a Thar 1L extraction plant and the optimum conditions were scaled to a Separex 2x16L pilot plant, both fitted with comprehensive energy monitoring devices. The yield varied from 37 to 97% of the one obtained for n-heptane. The energy consumption in both extraction plants allowed an analysis of the different components involved in the extraction process, namely pumping, heating and cooling. This energy consumption was analysed depending on the amount of $CO_2$ used, so the calculations can be extrapolated to any supercritical fluid extraction process undertaken in those plants. In the particular case of the supercritical extraction of oil seed rape, the best conditions in our experimental range were achieved at 55MPa and 35 °C, yielding 100.3 g of oil per kWh. This yield was comparable to that obtained in the pilot plant of 97.4 g oil/kWh. An accurate energetic evaluation of the extraction process at different scales has provided further evidence to encourage the change to supercritical fluid extraction as an economically viable industrial process.

## INTRODUCTION

The supercritical fluid extraction of oil seed rape is potentially a large scale application of this technology that has been thoroughly studied [1,2] and modelled [3], but still has not been industrially applied. The traditional extraction process includes mechanical pressing extraction and extraction with organic solvents, while the solid residual matrix is used as animal feed. The organic solvent is normally hexane, leading not only to toxicity problems in both the residual matrix and in the extract, but also needing a further purification step. Hexane has been recognised as a hazardous air pollutant by the US EPA and it has been reported by the EPA Toxic Release Inventory that more than 20,000 tonnes of hexane are released to the atmosphere each year from the extraction of vegetable oils [4]. Although extraction with hexane has a lower unit cost than extraction with supercritical $CO_2$ ($scCO_2$), production costs increase as extra refining steps and energy input is needed to reduce solvent residues to meet legally enforced maximum residue levels and to recover the solvent [5].

The advantages of supercritical fluid extraction against conventional extraction methods are clear: shorter extraction times, avoidance of toxic solvents and solvent residues and purity of the final product. In particular, $scCO_2$ results ideal due to its non toxic nature and affordable processing conditions (near ambient critical temperature, low price and inertness). Several oleaginous plants have been extracted with $scCO_2$ such as soybean, corn, wheat germ, sunflower seeds, safflower seeds or peanuts [6]. Some other supercritical extractions have been even economically evaluated with supercritical fluids [7]. However, there is scarce literature handling with the energetic evaluation of those processes.

The main industrial drawback of the supercritical extraction is the reluctance of industry to adopt new technologies. This technophobia combines with the current economic constraints on capital investment creating a difficult barrier to surpass. However, an accurate energetic evaluation of the extraction process at different scales could provide the needed information to encourage the change to supercritical technologies.

If the consumed energy per kg of $CO_2$ is used as a measuring unit, the energetic evaluation of any supercritical extraction in a certain extraction plant can be taken into account. Furthermore, if the yield is then introduced as a variable for a specific case, the energetic viability of such process can be inspected.

The aim of this work is to evaluate the supercritical $CO_2$ extraction of rape seed oil and its energy consumption in two different scales. The influence of pressure (25-55 MPa), temperature (35-75 °C) and flow rate on the extraction yield and energy consumption was analysed.

## MATERIALS AND METHODS

### Raw material

Oil seed rape seeds, *Brassica napus* (Syngenta variety NK Grandia), were harvested from farms in north Wales (Flintshire, Denbighshire and Anglesey) and west Cheshire and supplied by Blodyn Aur (Corwen, Wales, UK). Seeds were crushed twice with a roller mill (BDC Systems Limited, United Kingdom) with a tolerance of 1mm. The seeds were freshly crushed prior to each of the extractions to avoid oil degradation. $CO_2$ was provided by BOC gases.

### Extraction equipment

The experiments were carried out in the $CO_2$ laboratory of the Biocomposites Centre in Bangor University. The optimization of the process was accomplished in the 1L extraction plant while the scaling up was accomplished in the 2x16L pilot plant.

The optimisation of the extraction was carried out in a 1L plant extractor (Thar Technology, Pittsburgh, PA, USA) with two separators (0.5 L and 0.25 L capacity) and computerized control of temperature and pressure. Its working limits are 60.0 MPa and 90 ºC. The heating in the system is accomplished by electric resistances while the cooling is accomplished by a Neslab RTE10 bath. The sapphire piston pump (P-200A) works with a maximum $CO_2$ flow rate of 12kg/h. The energy consumption is recorded by two systems: plug-in monitors (2000MU, Prodigit Electronics) and a real time energy data capture system. The latter is provided by Enistic Energy Management Systems, which uses individual current clamps and sensors in conjunction with a smart box and controller. The controller passes the data to the Enistic servers where it can be accessed online [8] and further analysed.

The scaling up of the extraction was conducted in a 2x16L extractors pilot plant (Separex, France) with two separators (1 L capacity) with computerized control of temperature and pressure and automatic sampling. It can be seen in Figure 1. Its working limits are 70.0 MPa and 80 ºC and it has a recirculating system for the $CO_2$. The heating in the system is accomplished by a water recirculating system powered by a heater (Vulcatherm H2100). The cooling is accomplished by a chiller (Hitema C2000). The metallic piston pump (P200 LGP D26) works at a maximum flow rate of 50 kg/h. The energy consumption and metrics of the different components is collected by the software.

**Figure 1.** Separex Pilot Plant for Supercritical Fluid Extraction

Pressures ranged from 25.0 MPa to 55.0 MPa and temperatures from 35 ºC to 75 ºC. $CO_2$ flows ranged from 2.4 kg/h to 7.2 kg/h for the small plant pump and 40kg/h for the pilot plant pump. The separators conditions in the small plant were: separator 1, 1.0 MPa and 45 ºC ; separator 2, atmospheric pressure and 25 ºC. The separator conditions in the pilot plant were : separator 1 8.0 MPa, 45 ºC; separator 2, 5.0 MPa, 25 ºC.

The experimental procedure is the following. The extractor is packed with crushed seeds (0.66 kg and 9.78 kg in the small and the pilot plant respectively). The $scCO_2$ enters the extractor in such conditions due to the chiller that allows the pressurization of the liquid in the pump and due to the inline pre heater before entering the extractor. Once the pressure and working temperatures are reached in the extractor and separators, the extraction time begins. Pressure in the vessels is controlled by the automatic back pressure regulators. The extracted oil is collected every hour (in the small scale) or every 60 seconds (in the pilot plant, thanks to the automatic sampling). The extraction was halted when the experiment was entering in the asymptotic phase, coinciding with a recovered amount of oil in the hourly fraction smaller than 5% of the extractable oil.

Soxhlet extractions with n-heptane were carried out as a comparison.

## RESULTS

### Extraction experiments

A set of 14 experiments was planned in the range of 25-55 MPa, 35-75 °C and 2.4-7.2 kg/h in the 1L extraction plant to determine the best extracting conditions. The experiments can be seen in the Table 1 together with their yields.

**Table 1.** Experimental runs for the optimization of the supercritical extraction

| # | P (MPa) | T (°C) | Flow (kg/h) | Kg CO$_2$/kg seed | Y (%) | Ycut-off (%) |
|---|---|---|---|---|---|---|
| 1 | 25 | 75 | 4.8 | 69 | 38.2 | 19.9 |
| 2 | 25 | 55 | 4.8 | 69 | 57.7 | 24.5 |
| 3 | 25 | 35 | 4.8 | 69 | 78.5 | 31.1 |
| 4 | 35 | 75 | 4.8 | 69 | 69.9 | 37.5 |
| 5 | 35 | 55 | 4.8 | 69 | 84.5 | 57.8 |
| 6 | 35 | 35 | 4.8 | 69 | 94.0 | 54.7 |
| 7 | 45 | 75 | 4.8 | 36 | 80.0 | 71.3 |
| 8 | 45 | 55 | 4.8 | 51 | 96.7 | 77.7 |
| 9 | 45 | 35 | 4.8 | 51 | 95.9 | 67.9 |
| 10 | 55 | 75 | 4.8 | 29 | 88.1 | 85.4 |
| 11 | 55 | 55 | 4.8 | 29 | 88.6 | 83.7 |
| 12 | 55 | 35 | 4.8 | 36 | 95.0 | 88.1 |
| 13 | 55 | 75 | 2.4 | 22 | 72.4 | 60.3[a] |
| 14 | 55 | 75 | 7.2 | 29 | 87.9 | 82.9 |

**Y (%):** Yield percentage respecting to the heptane extraction

**Ycut off (%):** Yield percentage respecting to the heptane extraction at the cut-off point (21.8 kgCO$_2$/kg raw material). [a] cut-off point taken at 3 hours of extraction

The yields for the supercritical experiments, ranging from 38 to 96 %, have been expressed as percentage of yield of a Sohxlet n-heptane extraction. This n-heptane yield was 46 grams oil/100 grams of crushed seeds. The supercritical extraction curves are shown in Figure 2, where the cumulative extraction yields are plotted against the amount of CO$_2$ used.

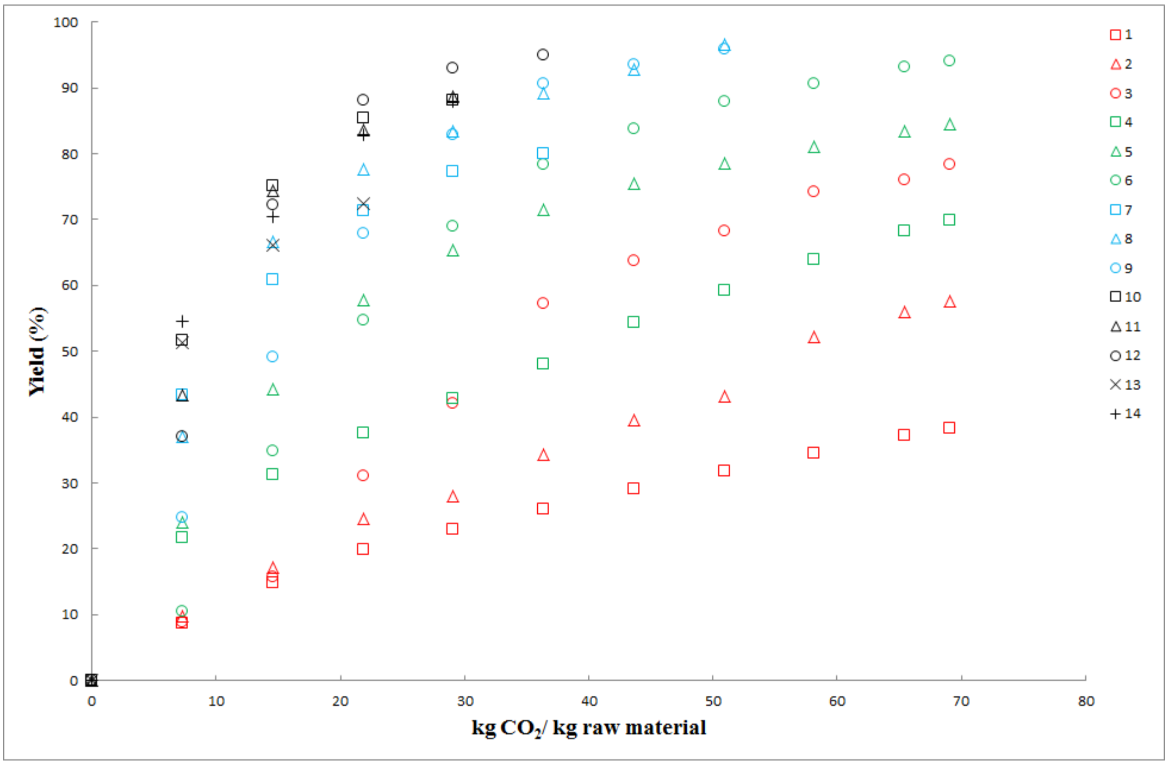

**Figure 2.** Extraction curves. kg CO$_2$/kg raw material vs Yield (%). Numbers correspond to the experimental conditions in Table 1. Shortcut: 25.0 MPa, 35.0 MPa, 45.0 MPa, 55.0 MPa.□: 75°C, Δ: 55°C, ○:35°C. x: 2.4 kg/h, +:7.2kg/h

Observing the extraction curves in Figure 2, where the extraction yield is represented against the $CO_2$ amount, it has been chosen a cut-off point to stop the extraction. This cut-off point corresponds to the change in the tendency of the extraction curve. From this point onwards, the extraction rate is not influenced by the solubility of the oil in the supercritical fluid, but by the internal diffusion of the oil in the seeds. The cut-off point was chosen at 21.8 kg$CO_2$/kg raw material, corresponding to three hours of extraction at the normal $CO_2$ flow of 4.8 kg/h. The extraction yields at the cut-off point are represented against the temperature and pressure in Figure 3.The trends for the different pressures can be clearly seen.

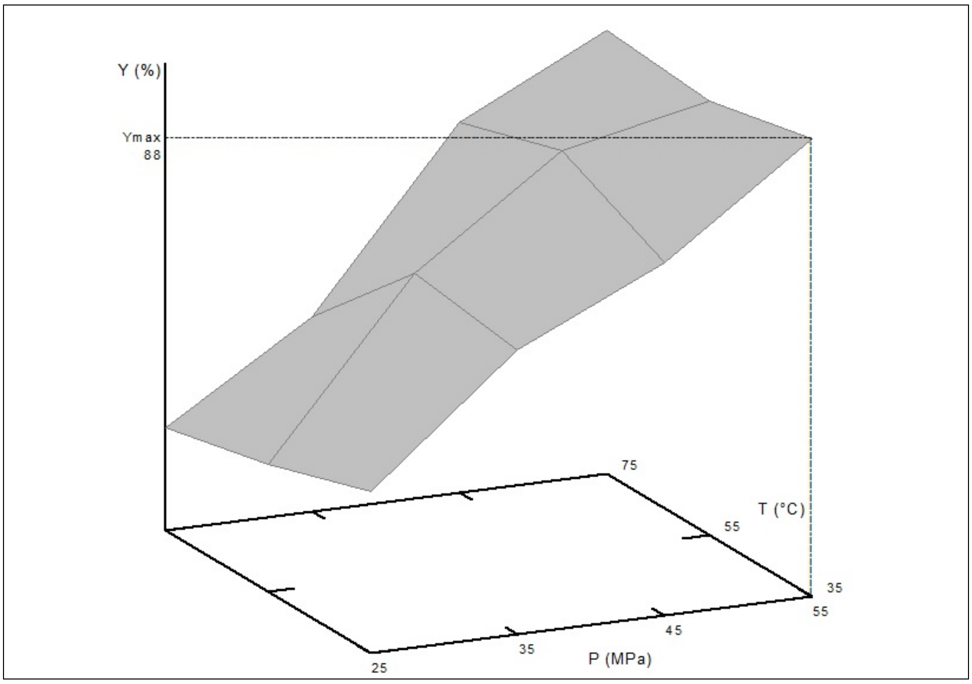

**Figure 3.** Extraction yields at the cut-off point for experiments 1-12 conducted in the small scale plant. Flow rate: 4.8kg/h. Extraction time: 3 hours. Kg $CO_2$/kg raw material=21.8.

The yields at lower pressures, i.e 25-35 MPa, are significantly different for the studied temperatures. However, as the pressure increases, the yields for the different temperatures become similar to each other, needing an energetic evaluation of the extraction to find out the optimum conditions to reproduce in the higher scale. The energetic evaluation, which will be explained in the next section, pointed out that the best conditions in the studied range for the scale up were 55.0 MPa and 35 °C. The results of the scale up are showed in Table 2. Similar results can be seen for both experiments. The slight difference between the yields in the small scale and the pilot scale can be explained because of the different ratio $CO_2$ flow rate/kg raw material in both extractors. A higher flow rate ratio determines a higher yield for the same extraction time.

**Table 2.** Comparison between small and big scale extraction trials

| # | P (MPa) | T (°C) | Kg $CO_2$/kg seed | Y (%) | Kg $CO_2$/kg seed at cut-off point | Ycut-off (%) | Kg $CO_2$/kg seed·h ($h^{-1}$) |
|---|---|---|---|---|---|---|---|
| 12 | 55 | 35 | 36 | 95.0 | 22 | 88.1 | 7.3 |
| PILOT | 55 | 35 | 26 | 87.0 | 18 | 74.5 | 4.1 |

## Energetic evaluation of the supercritical extraction

As a key part of the sustainability and feasibility of an extraction process, the energy consumption is a crucial factor that has to be taken in to account. Bearing this in mind, the used energy during the extractions was screened and analysed for all of the experiments. In the small scale plant, the energy screening is conducted with both the Enistic service (see material and methods) and plug-in monitors. In the pilot plant, the energy measurement is collected by the software. The energy involved in a certain supercritical extraction process for a given extraction plant can be represented as a function of energy used per kilogram of $CO_2$. In such case, the energy consumption can be seen in the following Figure 4.

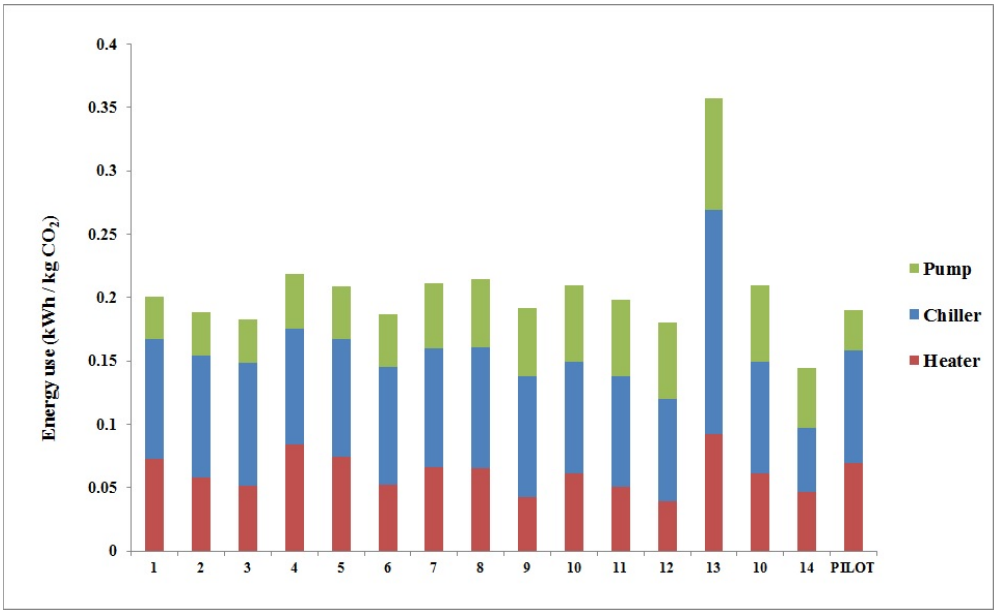

**Figure 4.** Energy used per kg $CO_2$. Each component shown in different colour.

It can be seen that the energy use per kilogram of $CO_2$ is similar for all the cases in which the flow rate is the same. The energy used per kg $CO_2$ is slightly higher for higher temperatures, while it remains unchanged for different pressures. If the flow rate is lowered, the increase of energy is patent due to the increase of the extraction time (Experiment #13). On the contrary, the higher the flow, the lesser the energy (Experiment #14). The efficiency of the pilot plant is comparable to that of the small scale plant. This behaviour is general for all the extractions undertaken in these two extraction plants. Knowing this behavior, the importance of optimizing the extraction conditions has to be highlighted. If the yield of the extraction is included, the energetic details of the process for the supercritical extraction of oil from rapeseed oil seeds appear in figure 5.

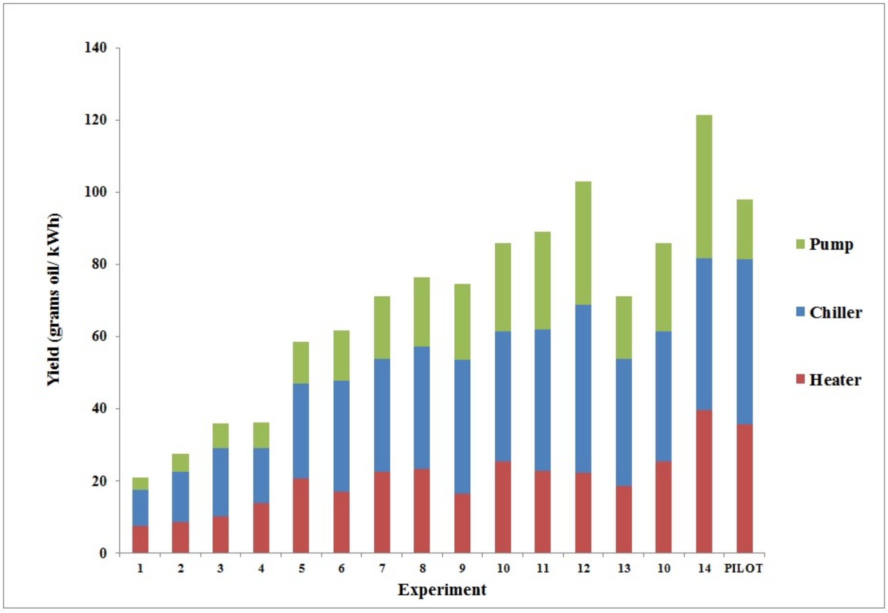

**Figure 5.** Grams of oil obtained per kWh. Each component shown in different colour.

It can be seen that for a given pressure,the yield of the extraction per kWh is higher at lower temperatures. It can also be seen that when pressure is increased, the yields of oil per kWh are higher. Those two trends indicate that the increase of solvent density effect is higher than that of the increasing volatility of the extractable material.

The comparison of energetic yield for the small and pilot plants in the same conditions can be seen in Figure 6.

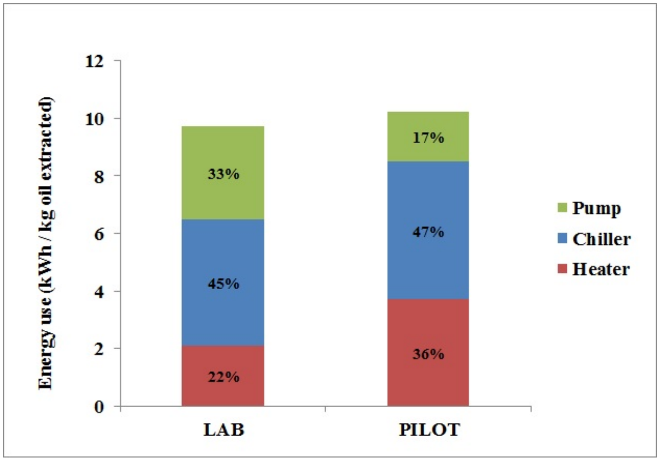

**Figure 6.** Grams of oil obtained per kWh. Comparison between small and pilot scale. Each component shown in different colour.

Despite the different design of the plants, the energy efficiency for both is similar. The small scale plant uses 9.7 kWh to extract 1 kg of oil, while the pilot plant needs 10.2 kWh. The energy distribution between the components varies because of the different systems used for both plants (heating through water jackets in the pilot plant while heating through electrical resistances in the small scale). The chiller in the pilot plant has a higher proportion of energy consumption, due to the cooling needs to recycle the $CO_2$, although the 2% difference cannot be explained only by this fact. The pump usage of energy is higher in the small scale. This can be explained by the overdimensioning of the pump for this purpose in the small scale (maximum flow rate of 12 kg/h while in the experiment 4.8 kg/h are used). On the other hand, the pump in the pilot scale is working almost at its full capacity. It has to be pointed out that although the energy efficiency of the pilot plant is slightly lower, this plant is operating with recirculating $CO_2$, which includes a further energetic requirement that the small plant does not have.

## CONCLUSION

The supercritical extraction of oilseed rape has proved to be an alternative to the conventional organic-based extraction method using n-hexane. The scale up of the supercritical process was successfully accomplished from 1L to 16L using a small and a pilot plant respectively. The optimum conditions in the studied range were 35°C and 55.0 MPa. The overall yield of this extraction was 95% of the one obtained with n-heptane, while the yield at the cut-off point was of 88%. An extraction cut-off point was established for the different experiments to optimise the energy use during the extraction, resulting in 21.8 kg/h of $CO_2$ per kg of raw seeds. The yields in the pilot plant (87 and 74% respectively) were similar to the ones of the small scale.

The energy needs in both plants were recorded during the extraction. If the yield of the extraction is not included, the energy used per kg of $CO_2$ has been calculated for different conditions, showing an average value of 0.19 kWh/kg $CO_2$ for the small scale at 4.8 kg/h. If the flow was changed, this value changed to 0.36 and 0.14 kWh/kg $CO_2$ for 2.4 and 7.2 kg/h respectively. In the pilot plant, this value is 0.19 kWh/kg $CO_2$.

If the yield is taken into account, the energy needed to extract 1 kg of oil in the small plant in its optimum conditions was 9.7 kWh, while in the pilot plant was 10.2 kWh. The energy distribution shows different usages due to the different elements in the plants. The higher energy consumption per kg of extracted oil in the pilot plant can be explained by the recirculation of the CO2, as it introduces a further energy consumption step in the process.

The scale up and the energetic evaluation of a supercritical extraction have improved the understanding of the process and they have become a useful tool to make decisions towards its industrial application.

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