

ECONOMIC OPTIMIZATION OF SOLVENT CYCLE CONDITIONS FOR THE SUPERCRITICAL CO₂ EXTRACTION OF PREPRESSED OILSEEDS AT INDUSTRIAL SCALE

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Abstract. Supercritical CO₂ (scCO₂) extraction at industrial scale is typically done in plants with two or more extraction vessels with solvent recycling capabilities. The solvent cycle consists of a buffer tank (where the CO₂ is stored as a saturated liquid), a pump, a throttling valve (where the CO₂ stream with solute is expanded up to separation conditions), a separation vessel, and different heat exchangers to adjust the temperature of the CO₂ stream to the required compressing, extraction, and separation conditions. To improve the economy of the solvent cycle the operational conditions in the different steps can be optimized to allow saves in energy and/or CO₂. The objective of this work was to study the operational conditions for the separation step (temperature, T , and pressure) and for the buffer tank (different temperatures at saturation pressure) in the solvent cycle and to evaluate its impact in the costs of oil extraction from 2-mm particles of prepressed rapeseed extracted at 40 °C and 30 MPa in a 2×1-m³ scCO₂ extraction plant (vessels with a length-to-diameter (L/D) ratio of 4.5) using a superficial CO₂ velocity of 6.7 mm/s. In this work the operational conditions considered in the separation vessel were 5, 6, and 7 MPa for $T > T_s$, (where T_s is saturation temperature). The temperatures considered for the buffer tank were 5, 15, and 25 °C and saturation pressure. To determine the separation between oil and CO₂ we simulated the vapor-liquid-equilibrium of the binary system using the GC-EoS. The CO₂ losses in the separation step represented up to 25% w/w of the extracted oil. The best combination of the operation conditions was separation at 7 MPa and 30 °C, and buffer tank 15 °C reaching a 4% in saving costs.

Keywords: prepressed oilseeds; separation and buffer tank conditions; supercritical CO₂ extraction; industrial scale.

1. Introduction

Supercritical carbon dioxide (scCO₂) extraction at industrial scale is typically carried out in plants with two or more extraction vessels (to avoid dead times in the extraction process) allowing a practical continuous extract production and improving the usage of the CO₂ [1]. Industrial plants also have recycling capabilities where the CO₂ is recirculated to the process by adjusting operational conditions in a solvent cycle [2].

Potential users of this technology think that supercritical extraction is too expensive comparing with traditional ones (*e.g.*, solvent extraction), due mainly to the high investment costs [3]. Furthermore, in literature there are few works that studying systematically the economics in supercritical processes at industrial scale. Most works estimate costs for particular cases of specific products [4]. Therefore, it is difficult to point out emphatically that supercritical extraction is a non-competitive technology without a deeper cost analysis.

Regarding to cost estimation, del Valle *et al.* [4] showed the convenience of process simulation to analyze the costs in a supercritical extraction process, where operational parameters (*e.g.*, mass flow rate of CO₂ or superficial velocity, particle size of the packed bed, number of extraction vessels, among others) were changed in a wide range. They used the algorithm proposed by Núñez *et al.* [1] to simulate the mass transfer in the extraction process and determine the annual productivity in an industrial plant processing rapeseeds with scCO₂ at 40 °C and 30 MPa. In particular, they studied the effect of estimated particle size (0.5, 1, 2, 3, and 4 mm), superficial velocity of CO₂ ($U = 2.75, 5.50, \text{ or } 11.0 \text{ mm/s}$), and number of extraction vessels (2, 3, or 4) on the operational cost of an installed plant with idle capacity. Finally, they estimated USD 4.1/kg oil as the lowest operational cost for the extraction of 2-mm particles using a superficial velocity of CO₂ of 2.75 mm/s in a four-vessel plant.

On the other hand, Núñez and del Valle [5] studied the effect of geometry of extraction vessels (aspect ratio, $3 \geq L/D \geq 8$), superficial CO₂ velocity ($2.71 \geq U \geq 10.4 \text{ mm/s}$), and number of extraction vessels ($n = 2, 3, \text{ or } 4$) on the production cost. This cost included the capital or investment in the plant itself (between USD 4.5 and 6.4 millions). The lowest estimated production cost was USD 7.808/kg oil for a mass flow rate of 6000 kg/h ($U = 10.4 \text{ mm/s}$) in a four-vessel plant (aspect ratio, $L/D = 6$). Their results showed that for value-added compounds the scCO₂ extraction could become commercially competitive depending on operational conditions.

In the cost analysis done by del Valle *et al.* [4] and Núñez and del Valle [5] the mass flow rate of CO₂ was the only parameter related with the solvent cycle that was changed. In all cases, the operational conditions in the separation vessel and the buffer tank from the solvent cycle were kept constant (60 °C and 8 MPa, and CO₂ at 25 °C as saturated liquid, respectively). So, it has not been studied nor quantified the effect of both separation and buffer tank conditions on the costs in a supercritical extraction plant at industrial level.

The objective of this work was to optimize the operational conditions in separation vessel and buffer tank in the solvent cycle of an industrial supercritical CO₂ extraction plant by process simulation. We simulated a scCO₂ extraction plant with two vessels (1 m³ each) processing prepressed rapeseed (particles of 2 mm) to determine its effect on production cost. In particular, we explored separation conditions at 5-8 MPa and 5-25 °C, and buffer tank conditions at 5, 15, and 25 °C (CO₂ as saturated liquid).

2. Problem statement and solution

This section describes the solvent cycle conditions studied in this work for an industrial plant for the extraction of rapeseed oil (packed bed with particles of 2 mm) at 40 °C and 30 MPa, using a mass flow rate of 6000 kg of CO₂ per hour. Then, it shows how is estimated the phase equilibrium of rapeseed oil-CO₂ system at separation conditions. Finally, it presents briefly the methodology to estimate production cost for the oilseed extraction in a scCO₂ extraction plant.

2.1. Operational conditions in the solvent cycle

The solvent cycle in an industrial scCO₂ extraction plant consists in the following steps (see steps in Fig. 1): (1-2) a buffer tank stores the CO₂ as saturated liquid to feed the cycle. The stream exiting from the tank is pre-cooled to avoid cavitation inside the pump; (2-3) the system is pressurized by a pump up to extraction pressure; (3-4) right after the pump, the CO₂ stream is heated or cooled depending on the extraction temperature desired; then, the CO₂ stream flows through the packed bed in the extraction vessels for the extraction process itself; after the extraction vessels, (4-5) the CO₂ stream is expanded in a throttling valve down to separation conditions. It is necessary to add heat to the CO₂ stream to counteract the Joule-Thompson effect (temperature diminishes drastically due to a rapid expansion of the CO₂) for avoiding low temperatures that could provoke undesirable precipitation of the solute before the separation vessel. Then, the solute is recovered in the separation vessel; finally, (5-1) the CO₂ as a gas is condensed and stored again in the buffer tank.

del Valle *et al.* [4] and Núñez and del Valle [5] varied the solvent cycle only changing the mass flow rate of CO₂ ($3 \leq F_{\text{CO}_2} \leq 12 \text{ ton/h}$) and keeping constant the operational conditions of other steps in the solvent cycle. In that works used the following operational conditions: buffer tank operating at 25 °C with CO₂ as saturated liquid (6.4 MPa as saturation pressure); extraction at 40 °C and 30 MPa, which affects the temperature adjustment of the CO₂ stream that comes from the buffer tank (under these extraction conditions, CO₂ stream should be cooled before the pump to avoid cavitation, and heated after the isentropic compression in the pump); separation at 60 °C and 8 MPa (the pressure drop between extraction and separation steps

markedly affects the energy requirement); finally, CO₂ condensing at practically the same pressure than buffer tank, *i.e.*, 6.4 MPa [1,4,5].

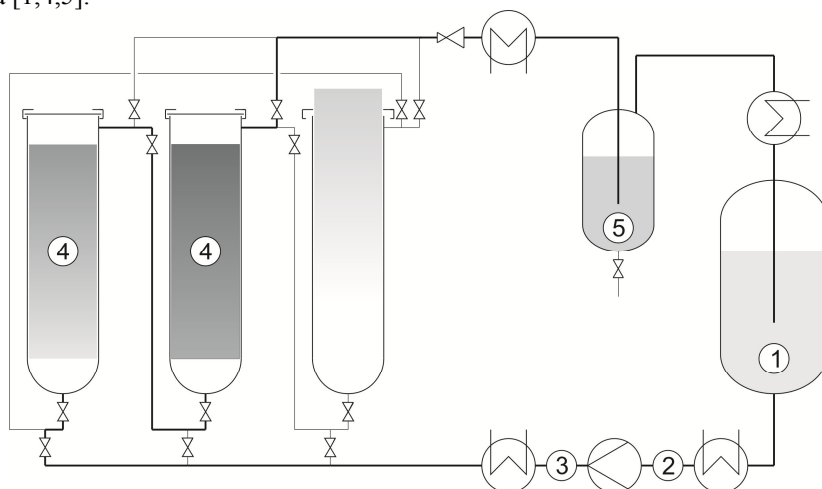


Figure 1. Solvent cycle in an industrial extraction plant with three extraction vessels connected in series. The cycle is indicated in bold line in the figure. The main equipment the following: (1) buffer tank; (2-3) pump; (4) extraction vessels; (5) separation vessel.

2.2. Selection of the operational conditions in the separation vessel and the buffer tank

Oil solubility in CO₂ at separation conditions should be minimum for allowing a practical complete separation. On the other hand, buffer tank conditions depend on operational conditions upstream in the cycle (separation vessel and condenser), and also affect to downstream steps in the cycle. When the temperature in the buffer tank decreases, the energy demand for cooling the CO₂ stream before the pump also decreases. This implies both operational and capital cost decrease (deeper analysis of capital cost is not included in this work). Considering all above, we explored a range of conditions that allowing us to minimize costs in the solvent cycle and the whole process as well.

Separation conditions are chosen such that oil recovery be maximum. In this step, two phases (gas and liquid) could form within the separation vessel, whose compositions are determined by the phase equilibrium between CO₂ and rapeseed oil. Gas phase corresponds to the oil solubility in CO₂, which indicates how much oil can be recovered. Liquid phase corresponds to the CO₂ solubility in oil, which indicates how much CO₂ is lost when the oil is sampled. In this work, we estimated the phase equilibrium for the rapeseed oil-CO₂ system using the GC-EOS [6,7,8].

Table 1 shows the separation conditions considered in this work. The combination 60 °C and 8 MPa is our base case because it was previously used [4,5]. We explored temperature-pressure combinations whose enthalpy (458.1 kJ/kg of CO₂ [11]) was equal to the base case as upper limit (we assumed pure CO₂ to estimate the physical properties of the stream given that oil concentration is very low). As lower limit we considered temperature-pressure combinations such that the CO₂ stream always keeps as gas.

Table 1. Operational conditions considered in this work for the separation vessel in the solvent cycle. Base case: $T = 60$ °C, $P = 8$ MPa.

Pressure (MPa)	Temperature (°C)	Enthalpy (kJ/kg of CO ₂)
5	15	419.8
	34.1	458.1
6	25	416.2
	43.6	458.1
7	30	392.7
	52.2	458.1
8	40	402.9
	60	458.1

On the other hand, buffer tank typically operates at environment temperature with CO₂ stored as saturated liquid, which defines the pressure inside it. In this work was considered three different operation temperatures in the buffer tank: 5, 15, and 25 °C (6.43, 5.08, and 3.97 MPa, respectively as saturation pressures). Finally, we assumed that the temperature in the buffer tank keeps constant along the extraction process.

2.3. Cost estimation for the extraction of rapeseed with supercritical CO₂

Operational costs in the SFE plant were divided in two categories: costs associated with solvent cycle and costs associated with the batch process. Costs associated with the solvent cycle correspond to the energy cost to pump, heat, cool, or condense CO₂, which are proportional to both mass flow rate of CO₂ and extraction time. Energy requirements in the solvent cycle were estimated using a *T-s* diagram for pure CO₂ similarly to del Valle *et al.* [4]. Costs associated with the batch process include the follow ones: cost of prepressed oilseeds (0.5 USD/kg, [9]); CO₂ make-up (0.4 USD/kg, [10]); and energy to depressurize and re-pressurize an extraction vessel (depending on extraction pressure and volume of extraction vessel). The amount of CO₂ loss at the ending of the extraction process was estimated with its density at 40 °C and 6.4 MPa (166.7 kg/m³, [11]) and the final porosity ($\varepsilon_T = 0.6$) resulting from the removal of oil. Finally, the costs associated with the batch process are the pressurization and depressurization of the extraction vessel (1m³ each), which were estimated in 0.669 and 0.221 USD per batch, respectively.

Also, the annual operational costs include the following other costs: labor of 53,000 USD/year-man [10] (two operators per 8-h shift, continuous operation); and other minor costs (administration, maintenance, and energy requirement of closure systems of extraction vessels, among others), which were assumed to account for 5% of the operational costs. Finally, we considered occupancy of 7200 h/year for the SFE plant.

Capital cost for the SFE plant was estimated with the expression proposed by Núñez & del Valle [5] (Eq. 1).

$$I = I_r \left(\frac{\alpha}{\alpha + 2\beta} \left(\frac{Q}{6000} \right)^{0.48} + \frac{\beta n f_p}{\alpha + 2\beta} \left(\frac{V_E}{1000} \right)^{0.48} \right) \quad (1)$$

where; *I* (USD) is the cost of purchase a SFE plant; α , β , and I_r are the parameters of the Eq. (1); I_r (USD) is the cost of a reference 2×1000 L SFE plant with a CO₂ pump capacity of 6000 kg/h; *n* is the number of extraction vessels; V_E (L) is the capacity of extraction vessels; f_p is the pressure correction factor, considering that a design pressure of 30% above the extraction pressure.

Finally, we estimated the production cost ($C_{\text{production}}$) as USD per kilogram of oil extracted using Eq. (2) considering the capital costs as an equivalent annual annuity (C_{capital} , USD/year, Eq. 3). Total oil extracted includes the remained oil at the end of the extraction, which is recovered when the extraction vessel is depressurized from extraction pressure to buffer tank pressure.

$$C_{\text{production}} = \frac{C_{\text{capital}} + 1.05 \times C_{\text{operational}}}{E_{\text{oil}}} \quad (2)$$

$$C_{\text{capital}} = \left[r \frac{(1-r)^a}{r^a - 1} \right] I \quad (3)$$

In Eq. (2), $C_{\text{operational}}$ (USD/year) is the annual operational cost including costs associated to both solvent cycle and batch process and labor (factor 1.05 indicates a 5% for minor costs); and E_{oil} (kg oil per year) is the annual productivity of the SFE plant. In Eq. (3) authors used a 10-year time horizon (superscript *a*) and a discount rate $r = 0.06$.

The minimization of production cost for two-vessel SFE plants was done by inspection of the curves of cost versus extraction time (not reported in this work). For three- and four- vessel SFE plants the minimal production cost was found by using the algorithm of del Valle *et al.* [1], where the optimum extraction time was determined in a 10-min interval in the curve of cost versus time.

3. Results and Discussion

Regarding to the separation step in the solvent cycle, Fig. 2 shows the liquid-liquid equilibrium for the rapeseed oil and CO₂ estimated with GC-EoS [6,7,8]. From this estimation we can determine the amount of CO₂ lost when the oil is sampled. According with this, the proportion of CO₂ lost every time that oil is sampled is in the range 15.5% (at 52.2 °C and 7 MPa) to 27.8% (at 15 °C and 5 MPa). In previous works [4,5], authors estimated the CO₂ loss in 20% w/w at 60 °C and 8 MPa from data reported by Klein & Schulz [12]. On the other hand, the oil concentration in the gas phase estimated by GC-EoS was zero for all separation conditions studied in this work. This implies that the CO₂ stream leaving the separation vessel does not drag oil to the buffer tank, allowing that CO₂ recirculates as solute-free to the cycle. This situation is desirable because the solvent power of CO₂ will be maximum in each cycle. All these results were used to estimate the CO₂ usage and its cost.

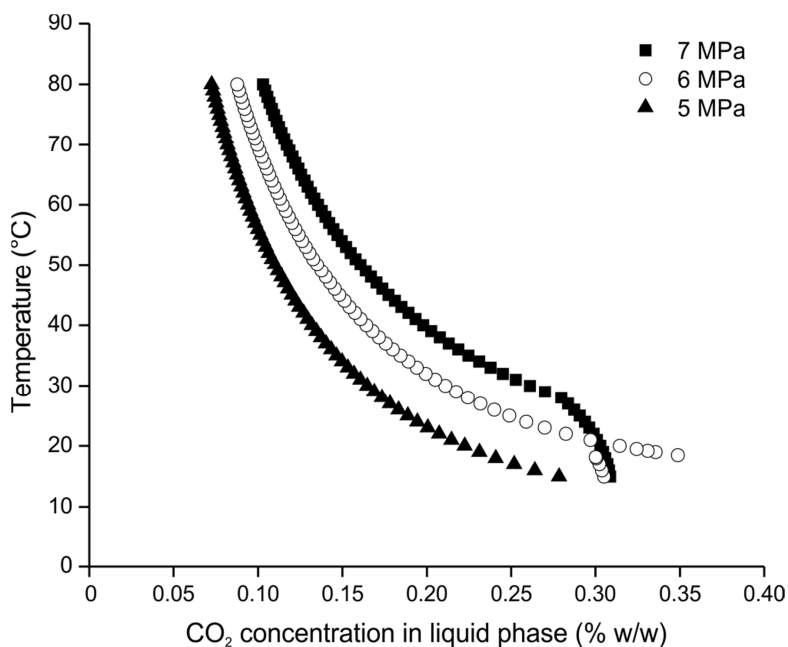


Figure 2. Liquid-Liquid equilibrium for the system rapeseed oil-CO₂

Fig. 3 shows the energy cost in the solvent cycle for each separation condition studied. In general, when the separation pressure keeps constant, the energy cost decreases when the separation temperature decreases. The lower and upper limits for energy costs are 25.9 USD/h (separation at 30 °C and 7 MPa, buffer tank at 25 °C) and 42.9 USD/h (separation at 60 °C and 8 MPa, buffer tank at 5 °C), respectively. The lower limit represents a decreasing of 27.4% respect the base case (separation at 60 °C and 8 MPa, buffer tank at 25 °C), which indicates an improvement of the economy in the solvent cycle. Also this result shows the convenience for operating the buffer tank to 25 °C (environment temperature).

Regarding of whole process costs, Table 2 presents the minimal production costs in the scCO₂ extraction plant (2×10^3 m³) processing 2-mm prepressed rapeseeds at described operational condition. The range of production cost estimated was 8.916-9.247 USD/kg of oil, for a narrow range of optimal extraction time (2.19-2.28 h) and annual productivity (260.3-264.3 ton of oil per year). The higher production cost was quite similar than the base case, which had a production cost estimated of 9.246 USD/kg of oil. The minimum production cost estimated was reached at the following conditions: 30 °C and 7 MPa for separation, and 15 °C for the buffer tank (note that this temperature does not coincide with optimal temperature in the buffer tank from the energy cost standpoint). On the other hand, the minimum production cost estimated in this work was 3.6% lower than base case, having both cases the same annual productivity (261.7 ton of oil per year). This implies that the savings in the process are exclusively attributed to the savings in the solvent cycle due to the change in the operational conditions in the separation vessel and the buffer tank.

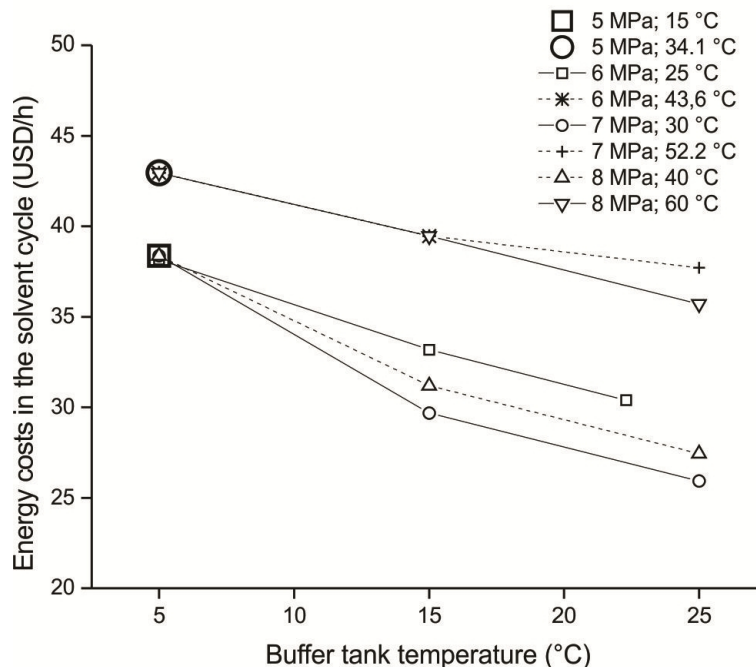


Figure 3. Energy costs (USD per hour) in the solvent cycle in function of separation and buffer tank conditions.

4. Conclusions

In this work we optimize the separation and buffer tank conditions in the solvent cycle of a supercritical CO₂ extraction from both energy and cost standpoint. In particular, we found the best combination for separation and buffer tank conditions in the solvent cycle of the extraction of 2-mm prepressed rapeseeds at 40 °C and 30 MPa in a plant with two 1m³-extraction vessels ($L/D = 4.5$), using a mass flow rate of 6000 kg/h of CO₂.

We considered a base case for separation and buffer tank conditions: 60 °C and 8 MPa; buffer tank at 25 °C, CO₂ as saturated liquid. From the energy cost standpoint, the best combination was separation vessel operating at 30 °C and 7 MPa, and buffer tank at 25 °C. This last result is according with the typical operation in an industrial plant, where the buffer tank is kept at environment conditions. On the other hand, we modeled the phase equilibrium for the system CO₂ and rapeseed oil using the GC-EOS. At the range of separation conditions studied in this work, there were not CO₂ losses in the sampled oil.

On the other hand, from the production cost standpoint, the best combination for separation vessel and buffer tank was 30 °C and 7 MPa, and 15 °C, respectively. Comparing with the base case, the production cost decreased 3.6%, which was due exclusively to the improvement in the economy of the solvent cycle because both processes had the same annual productivity.

Finally, the ongoing effort to optimize the economy in an industrial supercritical CO₂ extraction plant should be directed to two main goals: (i) to maximize the recovery of CO₂. This can be achieved by means of a compressor in a CO₂ recovery plant that communicates the extraction vessels and the buffer tank. Under this configuration it would be possible reaching near-atmospheric pressures; and (ii), to minimize dead times in the batch process, *i.e.*, when an extraction vessel is the reconditioning steps (given that supercritical extraction of solid substrates is a batch process, at the end of the extraction itself the exhausted substrate has to be replaced with a fresh one. So, reconditioning steps are the following: depressurization of the extraction vessel; unloading of exhausted substrate; loading of fresh substrate; and pressurization up to extraction pressure). Furthermore, it should pay special attention to the depressurization of an extraction vessel, which depends strongly on the heat transfer phenomenon during this stage.

Table 2. Production and energy costs in a scCO₂ extraction plant with two 1m³-vessels (aspect ratio, $L/D = 4.5$) processing 2-mm prepressed rapeseeds at 40 °C and 30 MPa, using a mass flow rate of 6000 kg/h of CO₂ ($U = 5.41$ mm/s) in function of operational conditions in separation vessel and buffer tank

Separation vessel		Buffer tank ^a		Energy cost (10 ³ ×USD/kg CO ₂)	Extraction time (h)	Productivity (ton oil/year)	Production cost (UDS/kg oil)	
Pressure (MPa)	Temperature (°C)	Temperature (°C)	Pressure (MPa)					
5	15	5	3.96	6.39	2.19	264.3	9.086	
	34.1	5	3.96	7.16	2.19	264.3	9.217	
6	25	5	3.96	6.39	2.19	264.3	9.086	
		15	5.09	5.53	2.22	263.0	9.017	
	43.6	22.3	6.05	5.07	5.07	2.25	261.7	9.044
		5	3.96	7.16	7.16	2.19	264.3	9.217
7	30	15	5.09	6.58	2.22	263.0	9.197	
		5	3.96	6.39	2.19	264.3	9.086	
		15	5.09	4.94	4.94	2.25	261.7	8.916
	52.2	25	6.43	4.32	4.32	2.28	260.3	8.964
		5	3.96	7.16	7.16	2.19	264.3	9.217
		15	5.09	6.57	6.57	2.22	263.0	9.197
8	40	25	6.43	5.95	2.25	262.7	9.247	
		5	3.96	6.39	2.19	264.3	9.086	
		15	5.09	5.20	5.20	2.25	262.7	8.964
	60	25	6.43	4.57	4.57	2.28	260.3	9.008
		5	3.96	7.15	7.15	2.19	264.3	9.217
		15	5.09	6.57	6.57	2.22	263.0	9.197
		25	6.43	5.95	2.25	261.7	9.246 ^b	

^a CO₂ as saturated liquid

^b Base case

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