

Oil Recovery Enhancement Through Supercritical CO₂



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Introduction

Oil recovery is a process that generates billions of dollars but not without extreme expenses. With the increasing global demand of energy, expenses will likely surge up. Therefore, approaches to mitigate the growing expense of oil extraction are constantly being sought after. Corporations, however, want an approach that that is not only cheap but can extract as much oil as possible. One approach has shown great promise in this regard: the extraction of oil through supercritical Carbon Dioxide (CO₂).

Supercritical CO₂ has many properties that should make oil extraction not only cheaper but more efficient. Not only is CO₂ cheap (\$40 a metric ton)¹ and abundant² but its liquid form is miscible with crude oil because it is nonpolar. When in a supercritical state, CO₂ also gains the ability to effuse through materials like a gas but dissolve them like a liquid. Therefore, the supercritical state of CO₂ is expected to significantly reduce the viscosity of crude oil and its surface tension with any solid the oil may come in contact with. Best of all, this will be done without changing the components of crude oil into new compounds. The stability of CO₂ and the fact that the critical point of CO₂ is not far from standard atmospheric pressure and temperature means supercritical CO₂ will not react or chemically change the composition of crude oil.

These properties make supercritical CO₂ particularly effective for oil extraction from deep reservoirs. A pressurized flow of supercritical CO₂ into oil reservoirs underneath the Earth's surface could reduce the viscosity of crude oil and the oil's surface tension with the rocks of the reservoir and the pipelines for which the oil is pushed out of. Allowing for a greater rate of oil extraction than from simply supplying a large enough pressure to push the oil out.

Although supercritical CO₂ seems like the perfect fluid for oil recovery, the viability of this approach must be tested. Therefore, the state parameters of CO₂ for a potential oil extraction experiment have been calculated through the Van der Waals equation of state. A respected equation for thermodynamic state functions due to the fact that it incorporates electrostatic forces and microscopic discrepancies for macroscopic volumes into its model. This paper represents the theoretical basis of supercritical CO₂ towards a hypothetical oil extraction experiment, with the actual experiment to be done in the future.

Index of Symbols

V=molar volume

T=temperature

P=pressure

ρ =molar density

Z=molar compressibility factor

V_c=critical molar volume

T_c=critical temperature

P_c=critical pressure

Z_c=critical molar compressibility factor

U=molar internal energy

H=molar enthalpy

S=molar entropy

A=molar Helmholtz energy

A_D= Density of Helmholtz energy

μ =chemical potential

R=universal gas constant= $8.314 \frac{\text{Joules}}{\text{mole} \cdot \text{Kelvin}}$

n=molar flow rate of CO₂

a= constant of attraction/repulsion between particles

b= constant of volume excluded by particles

C_v=isochoric heat capacity

C_p=isobaric heat capacity

ε=efficiency

Q=heat

t=time

Subscripts

i=initial

f=final

Procedures/Results

The critical parameters of CO₂ were calculated using the Van der Waals equation:

$$\text{Molar Van der Waals equation: } P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\text{Critical Criteria: } \left(\frac{dP}{dV}\right)_T = \left(\frac{d^2P}{dV^2}\right)_T = 0$$

$$(1) \left(\frac{dP}{dV}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} = 0$$

$$(2) \left(\frac{d^2P}{dV^2} \right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0$$

$$(\text{Substitution of 1 into 2}) \quad T_c = \frac{8a}{27Rb}, V_c = 3b$$

$$(\text{Substitution of } T_c \text{ and } V_c \text{ into molar Van der Waals}) \quad P_c = \frac{a}{27b^2}$$

$$(3) Z = \frac{PV}{RT}$$

$$(4) Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8}$$

The critical parameters of CO₂ were then used to calculate the a & b constants of the molar Van der Waals equation using two experimental values, P_c and T_c³:

$$\text{Experimental } T_c = 304.25 \text{ Kelvin}$$

$$\text{Experimental } P_c = 7.38 * 10^6 \text{ Pascals}$$

$$(\text{Substitution of } P_c \text{ into } T_c) \quad a = .366 \frac{\text{meters}^6 * \text{Pascals}}{\text{mole}^2}, b = 4.28 * 10^{-5} \frac{\text{meters}^3}{\text{mole}}$$

The calculated a & b were then used to calculate a predicted V_c to see if it came close to experimental values³:

$$\text{Calculated } V_c = 3b = 1.28 * 10^{-4} \frac{\text{meters}^3}{\text{mole}}$$

$$\text{Experimental } V_c = 9.40 * 10^{-5} \frac{\text{meters}^3}{\text{mole}}$$

*Note: During further calculations, the V_c used will be the one previously calculated, and the T_c and P_c used will be the experimental values. This allows the Van der Waals equation to follow the predicted values of a & b.

The stability criteria for a Van der Waals fluid of a pure-species system was then calculated:

$$(5) \text{ General Stability Criteria: } dS < \frac{dQ_{rev}}{T}$$

$$(TdS - dQ_{rev})_{T,V} = d(TS - U)_{T,V} = -dA < 0 \rightarrow dA > 0$$

$$\left(\frac{d^2A}{dV^2} \right)_T > 0 \rightarrow -\left(\frac{dP}{dV} \right)_T > 0 \rightarrow \left(\frac{dP}{dV} \right)_T < 0$$

$$(6) \text{ Molar Van der Waals Stability Criteria: } \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} < 0$$

The isochoric heat capacity⁴ was then integrated to be used to derive the thermodynamic state functions. The reference state for the integrations were assumed to be zero for simplicity:

$$(7) C_V = C_V^{ig} = C_P^{ig} - R = R \left(\frac{C_P^{ig}}{R} - 1 \right) = R(4.457 + 1.045 * 10^{-3}T - 1.157 * 10^5 T^{-2})$$

$$(8) \int C_V dT = R(4.457T + 5.225 * 10^{-4}T^2 + 1.157 * 10^5 T^{-1})$$

$$(9) \int \frac{C_V}{T} dT = R(4.457 \ln(T) + 1.045 * 10^{-3}(T) + 5.785 * 10^4 T^{-2})$$

The Thermodynamic State Functions for a pure-species Van der Waals fluid were then calculated. Again, the reference states were assumed to be zero for simplicity (i.e $U_i=0$, $S_i=0$, $T_i=0$, etc...):

(a) Molar Internal Energy

$$(a0) \left(\frac{dU}{dV} \right)_T = T \left(\frac{dS}{dV} \right)_T - p = T \left(\frac{dP}{dV} \right)_T - p = \frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = \frac{a}{V^2}$$

$$(a1) dU = \left(\frac{dU}{dT} \right)_V dT + \left(\frac{dU}{dV} \right)_T dV = C_V dT + \frac{a}{V^2} dV$$

$$(a2) \Delta U = \int C_V dT + \int \frac{a}{V^2} dV$$

$$(a3) U = U_i + \Delta U$$

$$(a4) U = R(4.457T + 5.225 * 10^{-4}T^2 + 1.157 * 10^5 T^{-1}) - \frac{a}{V}$$

(b) Molar Entropy

$$(b0) C_V = \left(\frac{dU}{dT} \right)_V = T \left(\frac{dS}{dT} \right)_V$$

$$(b1) \left(\frac{dS}{dV} \right)_T = \left(\frac{dP}{dT} \right)_V \text{ (Maxwell equation)}$$

$$(b2) dS = \left(\frac{dS}{dT} \right)_V dT + \left(\frac{dS}{dV} \right)_T dV = \frac{C_V}{T} dT + \frac{R}{V-b} dV$$

$$(b3) \Delta S = \int \frac{C_V}{T} dT + \int \frac{R}{V-b} dV$$

$$(b4) S = S_i + \Delta S$$

$$(b5) S = R(4.457 \ln(T) + 1.045 * 10^{-3}(T) + 5.785 * 10^4 (T^{-2})) + R \ln(V - b)$$

(c) Molar Helmholtz Energy

$$(c0) A = U - TS$$

$$(c1) A = \int C_V dT - \frac{a}{V} - T \int \frac{C_V}{T} dT - RT \ln(V - b)$$

(d) Molar Enthalpy

$$(d0) H = U + PV = U + \left(\frac{RT}{V-b} - \frac{a}{V^2} \right) V$$

$$(d1) H = \int C_V dT - \frac{2a}{V} + \left(\frac{RTV}{V-b} \right)$$

(e) Chemical Potential

$$(e0) \mu = H - TS$$

$$(e1) \mu(T, V) = \int C_V dT - \frac{2a}{V} + \left(\frac{RTV}{V-b} \right) - T \int \frac{C_V}{T} dT - RT \ln(V-b)$$

$$(e2)) \rho = \frac{1}{V}$$

$$(e3) \mu(\rho, T) = \int C_V dT - 2a\rho + \left(\frac{RT}{1-b\rho} \right) - T \int \frac{C_V}{T} dT - RT \ln\left(\frac{1-b\rho}{\rho}\right)$$

(f) Density of Helmholtz Energy

$$(f0) A_D(\rho, T) = \rho A = \rho \int C_V dT - a\rho^2 - \rho T \int \frac{C_V}{T} dT - \rho RT \ln\left(\frac{1-b\rho}{\rho}\right)$$

$$(f1) A_D(T, V) = \frac{A}{V} = \frac{\int C_V dT}{V} - \frac{a}{V^2} - \frac{T}{V} \int \frac{C_V}{T} dT - \frac{RT}{V} \ln(V-b)$$

A few of these functions were then graphed in order to analyze the thermodynamic properties of CO2 to make sure it was a suitable fluid for deep oil reservoir recovery. The spinodal and binodal were also graphed on a few of these diagrams using these equations:

1. Spinodal Criteria: $\left(\frac{dP}{dV} \right)_T = 0$
2. Binodal Criteria: $\int P dV = P_{sat}(V_g - V_l) \rightarrow RT \ln \left(\frac{V_g - b}{V_l - b} \right) + \left(\frac{a}{V_g} - \frac{a}{V_l} \right) = P_{sat}(V_g - V_l)$

Pressure-Volume diagram of CO₂

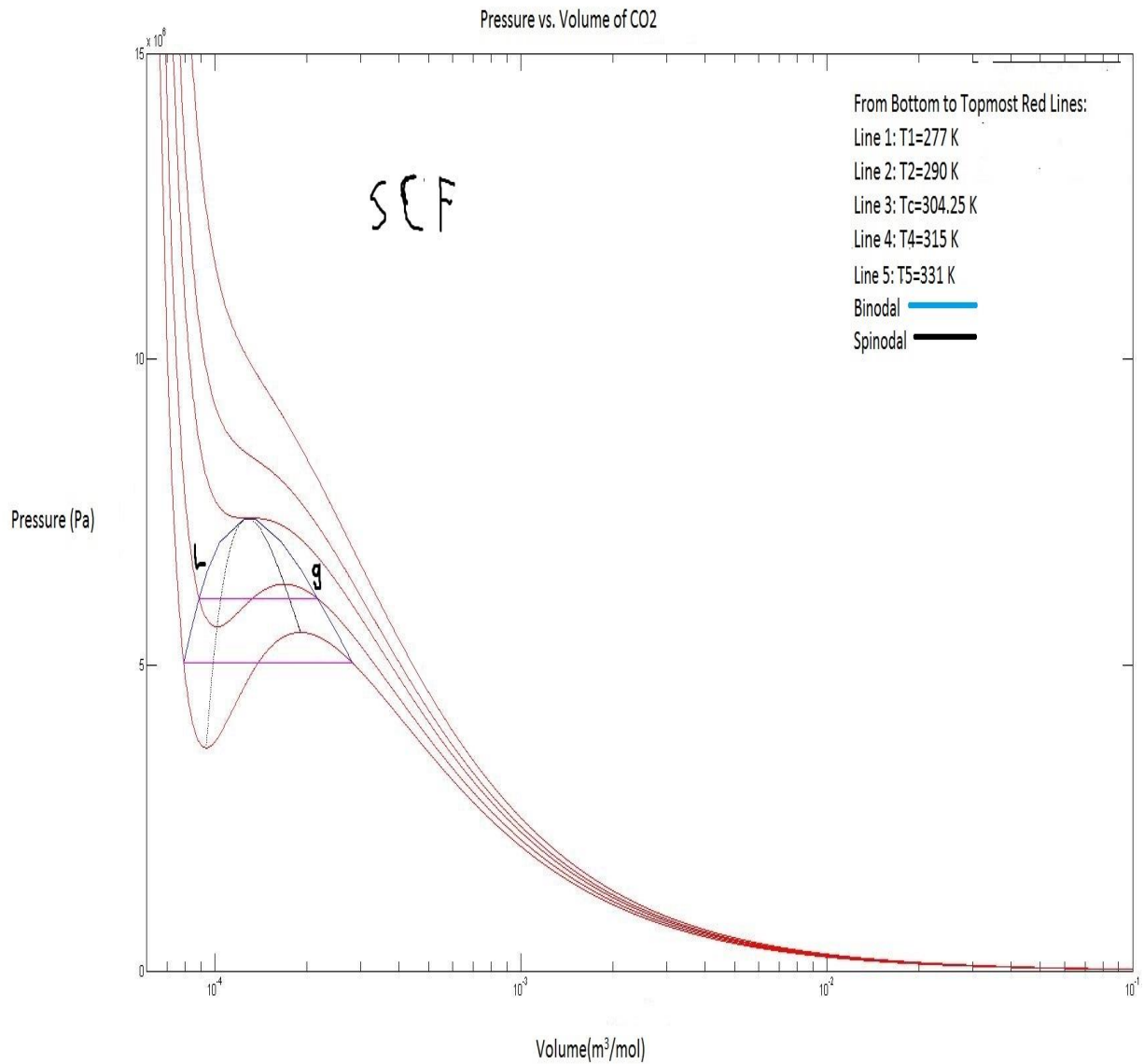


Figure 1: PV Diagram of CO₂

The graph contains a liquid (L), gas (g), and supercritical fluid (SCF) area. Note the figure follows Maxwell's equal area rule. The figure does not seem to upon first inspection simply because the x-axis is graphed over logarithmic intervals.

Saturation points were tabulated over six isotherms including the critical point:

| | $P_{sat}(\text{Pa})$ | $V_l^{sat}(\text{m}^3/\text{mol})$ | $V_g^{sat}(\text{m}^3/\text{mol})$ |
|---------------------------|----------------------|------------------------------------|------------------------------------|
| T1-277 K | $5.03 * 10^6$ | $7.92 * 10^{-5}$ | $2.83 * 10^{-4}$ |
| T2-283 K | $5.51 * 10^6$ | $8.30 * 10^{-5}$ | $2.51 * 10^{-4}$ |
| T3- 290 K | $6.09 * 10^6$ | $8.88 * 10^{-5}$ | $2.16 * 10^{-4}$ |
| T4- 295 K | $6.54 * 10^6$ | $9.46 * 10^{-5}$ | $1.92 * 10^{-4}$ |
| T5- 300 K | $7.00 * 10^6$ | $1.04 * 10^{-4}$ | $1.66 * 10^{-4}$ |
| T _C - 304.25 K | $7.38 * 10^6$ | $1.28 * 10^{-4}$ | $1.28 * 10^{-4}$ |

Table 1: Liquid-Vapor Volume Saturation Points of CO₂

Chemical Potential Diagram for CO₂

First the chemical potential for an isotherm was found before graphing:

$$\mu(\rho, T)_T = -2a\rho + \left(\frac{RT}{1-b\rho}\right) - RT\ln\left(\frac{1-b\rho}{\rho}\right)$$

Then, the chemical potential was realized to be $\Delta\mu$ since it was derived assuming the reference state was zero:

$$\Delta\mu_T = -2a\rho + \left(\frac{RT}{1-b\rho}\right) - RT\ln\left(\frac{1-b\rho}{\rho}\right)$$

Therefore, $\Delta\mu_T$, the difference between a new chemical potential and a **constant** original reference state of 0, of CO₂ was graphed at various isotherms:

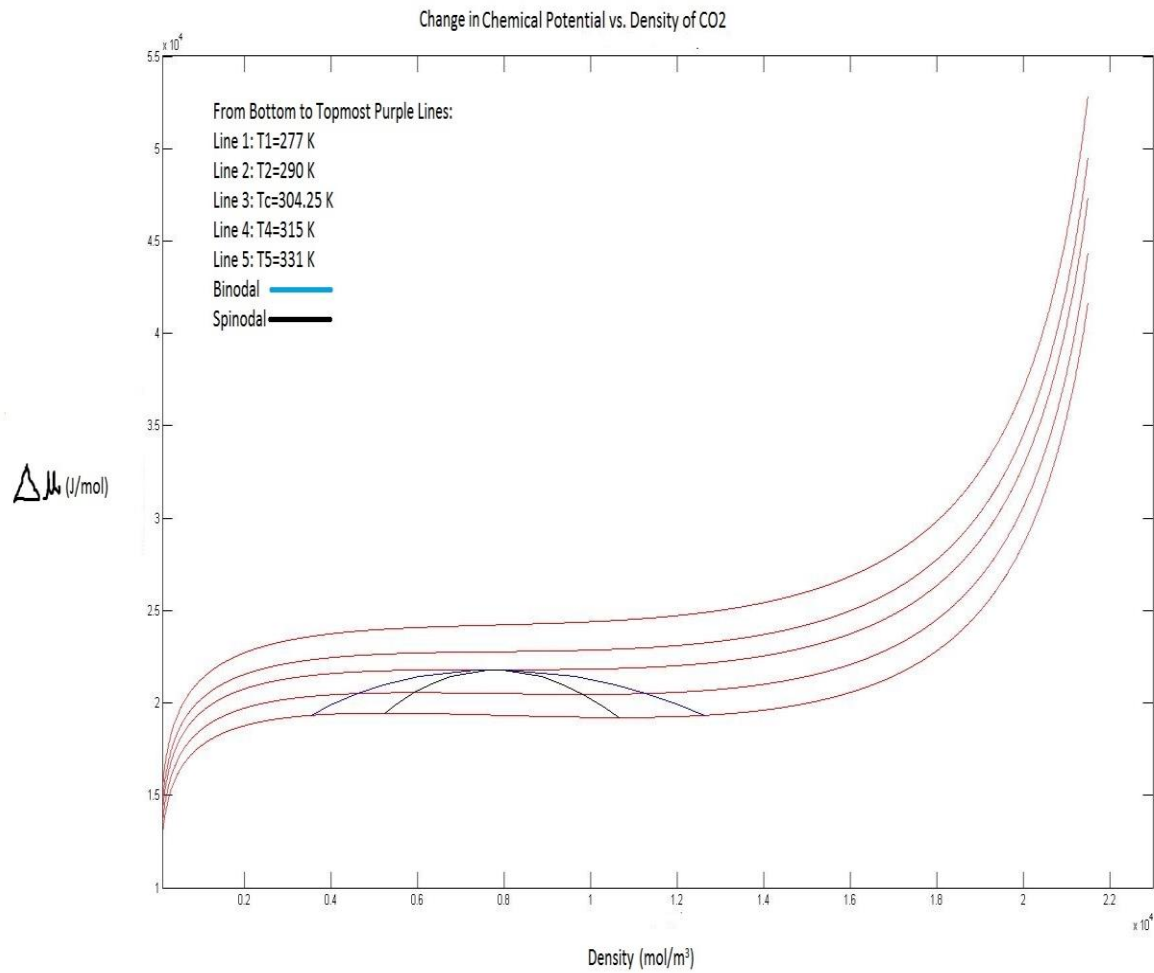


Figure 2: $\Delta\mu$ vs. Density Diagram at Various Isotherms

Saturation points were tabulated over six isotherms including the critical point:

| | $\rho_l^{sat}(\frac{mol}{m^3})$ | $\rho_g^{sat}(\frac{mol}{m^3})$ |
|--------------|---------------------------------|---------------------------------|
| T1-277 K | $1.26 * 10^4$ | $3.53 * 10^3$ |
| T2-283 K | $1.20 * 10^4$ | $3.98 * 10^3$ |
| T3- 290 K | $1.13 * 10^4$ | $4.63 * 10^3$ |
| T4- 295 K | $1.06 * 10^4$ | $5.21 * 10^3$ |
| T5- 300 K | $9.62 * 10^3$ | $5.21 * 10^3$ |
| Tc- 304.25 K | $7.81 * 10^3$ | $7.81 * 10^3$ |

Table 2: Liquid-Vapor Density Saturation Points of CO2

Helmholtz Energy Density Diagram for CO2

First, the Helmholtz energy density for an isotherm was found before graphing:

$$A_D(\rho, T)_T = -a\rho^2 - \rho RT \ln\left(\frac{1 - b\rho}{\rho}\right)$$

Then, the Helmholtz energy density was realized to be ΔA_D since it was derived assuming the reference state was zero:

$$\Delta A_D(\rho, T)_T = -a\rho^2 - \rho RT \ln\left(\frac{1 - b\rho}{\rho}\right)$$

Therefore, ΔA_D , the difference between a new Helmholtz density and a **constant** original reference state of 0, of CO₂ at 277 K was graphed:

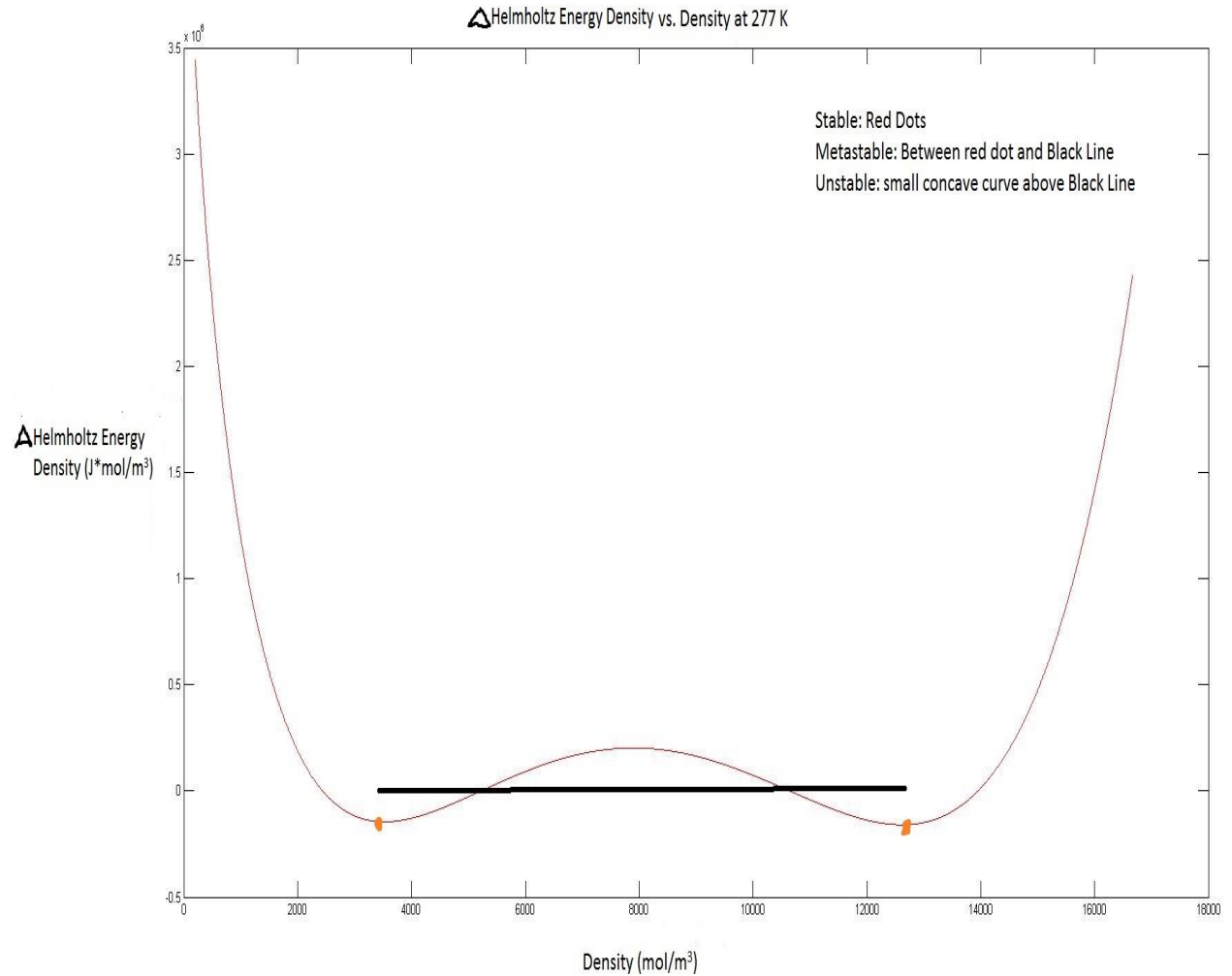


Figure 3: Change in Helmholtz Energy Density vs. Density

After a theoretical framework was formed for CO₂, a model to transform CO₂ gas, near standard atmospheric pressure and temperature, into a near-supercritical state was proposed. A state that would become supercritical with the added temperature increase of a deep oil reservoir. The proposed model was:

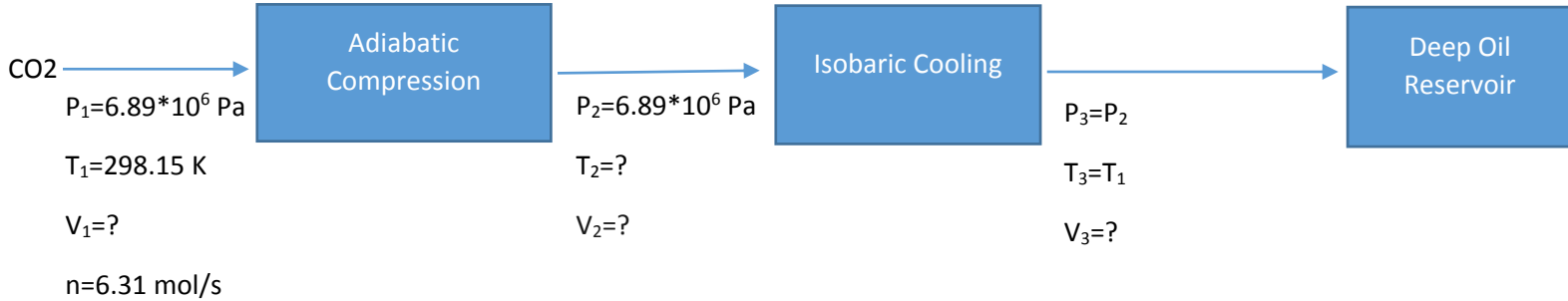


Figure 4: Transforming CO₂ Gas to Near-Supercritical State

The adiabatic compressor had an efficiency of .8 and the molar flowrate of CO₂ through the system was constant at 6.31 mol/s. The work and cooling requirements necessary for the proposed model were then calculated.

The equation for work necessary to push the system was derived through an energy balance of the energy going into the compressor minus the energy coming out. The total work of the system was simply the work of the compressor.

$$(10) W = nt[U_{in} + (PV)_{in} - (U_{out} + (PV)_{out})] = nt\Delta H_c$$

To find the enthalpy change of the compressor, a few parameters had to be worked out:

$$(11) P_1 = \frac{(RT_1)}{(V_1 - b)} - \frac{a}{V_1^2}$$

$$(12) V_1 = .0179 \frac{m^3}{mol}$$

$$(13) P_3 = \frac{(RT_3)}{(V_3 - b)} - \frac{a}{V_3^2}$$

$$(14) V_3 = 9.58 * 10^{-5} \frac{m^3}{mol}$$

$$(15) \Delta S_c = 0 = 8.314 \left[4.457 \ln \left(\frac{T_{2rev}}{T_1} \right) + 1.045 * 10^{-3} (T_{2rev} - T_1) + 5.785 * 10^4 (T_{2rev}^{-2} - T_1^{-2}) \right] + 8.314 \ln \left(\frac{V_{2rev} - b}{V_1 - b} \right)$$

(assumes adiabatic expansion of compressor with 100% efficiency)

$$(16) P_2 = \frac{(RT_{2rev})}{(V_{2rev} - b)} - \frac{a}{V_{2rev}^2}$$

$$(17) T_{2rev} = 637.8 \text{ K}$$

$$(18) V_{2rev} = 7.452 * 10^{-4} \frac{m^3}{mol}$$

The enthalpy change of the adiabatic compressor was taken by doing an isothermal and then isochoric path:

$$(19) dH = dU + PdV + VdP$$

$$(20) dP = \left(\frac{dP}{dT}\right)_V dT + \left(\frac{dP}{dV}\right)_T dV$$

Isochoric Path

$$(20) dH_V = C_V dT + VdP_V = C_V dT + V_1 \left(\frac{dP}{dT}\right)_V dT$$

$$(21) \Delta H_V = \int_{T_1}^{T_{2rev}} \left[C_V + \frac{RV_1}{V_1 - b} \right] dT$$

Isothermal Path

$$(22) dH_T = \frac{a}{V^2} dV + PdV + VdP_T = \frac{a}{V^2} dV + PdV + \left(\frac{dP}{dV}\right)_T dV$$

$$(23) \Delta H_T = \int_{V_1}^{V_{2rev}} \left(\frac{RT_{2rev}}{V - b} - \frac{RT_{2rev}V}{(V - b)^2} + \frac{2a}{V^2} \right) dV$$

Total Path

$$(24) \Delta H_C = \Delta H_T + \Delta H_V = 1.44 * 10^4 \frac{J}{mol}$$

The total work (over the interval of a second) & power required for the adiabatic compressor was then calculated:

$$(25) W_C = 9.12 * 10^4 \text{ J}$$

$$(26) Power_C = 9.12 * 10^4 \text{ W}$$

However, since the adiabatic compressor does not have 100% efficiency, the real work necessary for the compressor was calculated:

$$(27) W_{creal} = \frac{W_C}{\epsilon} = 1.14 * 10^5 \text{ J}$$

$$(28) \text{Power}_{creal} = 1.14 * 10^5 \text{ W}$$

The cooling requirement during the isobaric cooling was then calculated:

$$(29) Q_p = nt\Delta H_p$$

However, the only way to calculate ΔH_p was to get the true values for T_2 and V_2 based off the actual work requirement. Therefore, W_{creal} was substituted into equation 24, and T_2 and V_2 were substituted in place of T_{2rev} and V_{2rev} . T_2, V_2 , and P_2 were then substituted in the Van der Waals equation. After this system of equations was solved, the true values of T_2 and V_2 were found to be:

$$(30) T_2 = 709.5 \text{ K}$$

$$(31) V_2 = 8.4 * 10^{-4} \frac{m^3}{mol}$$

The heat loss required to cool CO2 over a 1-second interval was then found:

$$(32) dH_p = C_V dT + \frac{a}{V^2} dV + P_2 dV$$

$$(33) \Delta H_p = \int_{T_2}^{T_3} C_V dT + \int_{V_2}^{V_3} (\frac{a}{V^2} + P_2) dV$$

$$(34) Q_p = -1.49 * 10^5 \text{ J}$$

The total pathway looked like this:

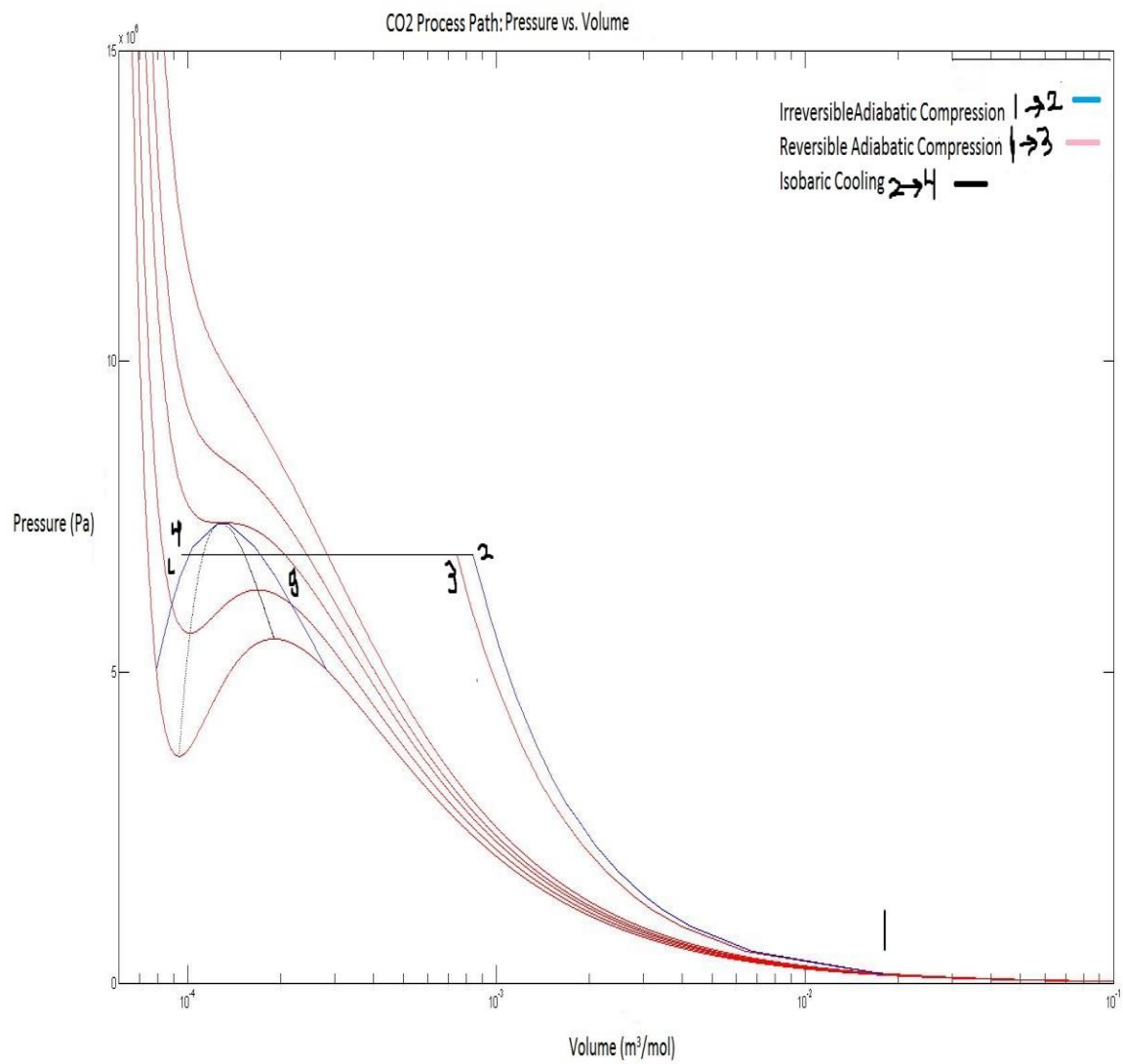


Figure 4: CO2 PV Process Path

The same pathway over an interval of pressure & temperature looked like this:

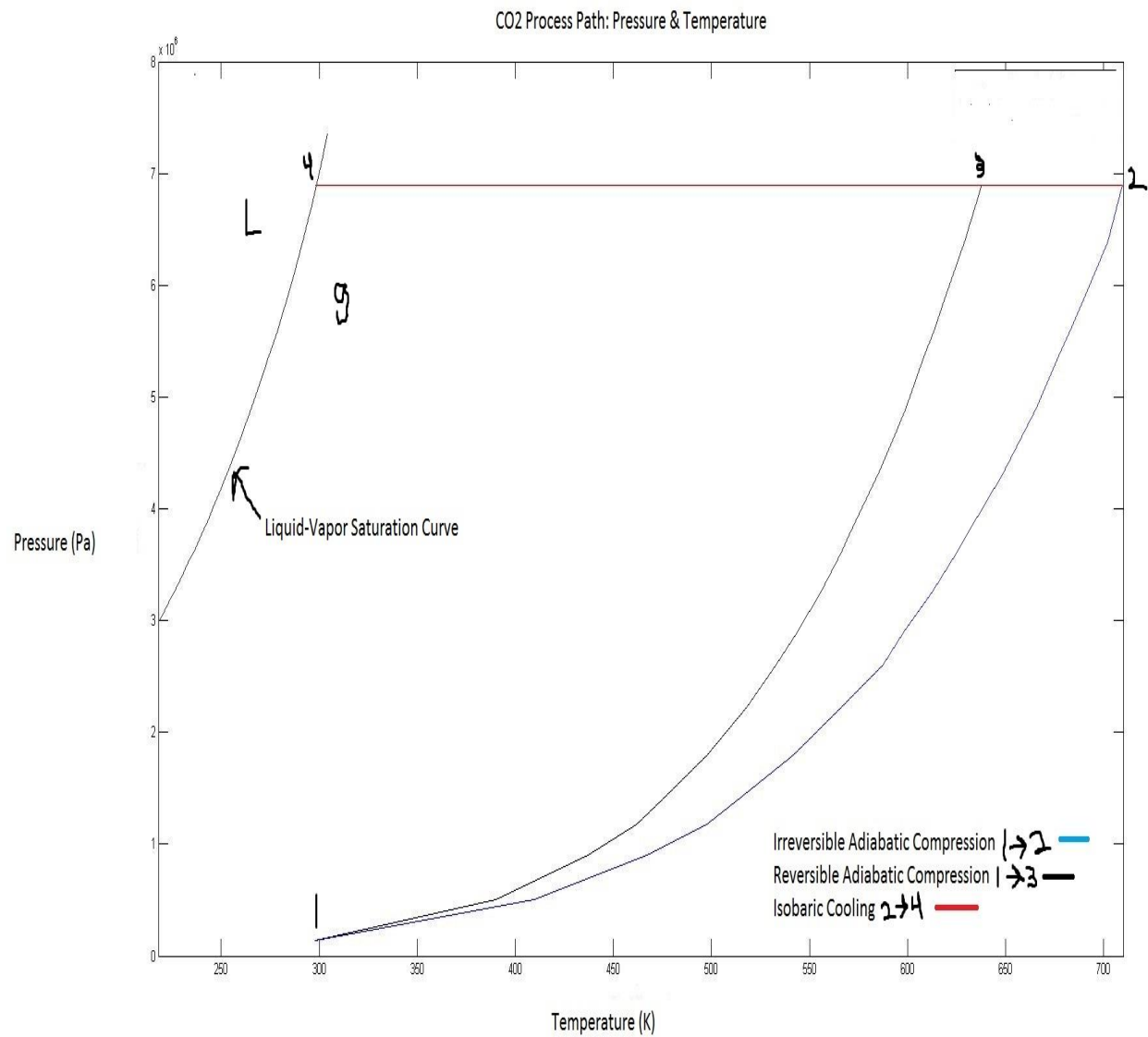


Figure 5: CO2 PT Process Path

Discussion

The proposed model was calculated to transform CO₂ gas to a liquid, but near-supercritical state, if the work supplied to the system was 1.14×10^5 J per second and the heat rate loss during isobaric cooling was -1.49×10^5 J per second. The PT and PV process diagram both verified that a liquid final state would be achieved as the process path was able to cross the vapor to liquid saturation curves of each diagram. Furthermore, the process diagrams confirm that with simply a slight increase of temperature and pressure, the final state of CO₂ can transform from a liquid to supercritical fluid.

As an added benefit, the chemical potential diagram predicts that this process will be largely spontaneous. As a liquid is changed into a supercritical fluid, the density sharply decreases. The diagram shows the change in chemical potential should be negative for sharp decreases in density. This gives a supercritical fluid the added bonus of stability. The fluid will not have the urge to leave the supercritical region back to liquid due to the Gibbs Free energy barrier in its way.

CO₂ also should have no trouble reaching its supercritical region for the oil recovery that this model was designed for, deep oil reservoir recovery. The depth and proximity to earth's mantle increases the pressure and temperature of CO₂ significantly as it travels towards oil⁵, naturally transforming it from a liquid to its supercritical state.

However, the proposed model has a few criticisms which must be mentioned. The Van der Waals equation of state predicted critical point volume is 1.28×10^{-4} m³/mol, larger than the experimental critical point volume of 9.4×10^{-5} m³/mol⁶. This discrepancy will cause there to be a small range of volumes that will not produce a supercritical fluid even if predicted by the Van der Waals equation. Also, the actual binodal and spinodal of the PV diagram would shift slightly to the left due to the smaller experimental volumes. This may cause our predicted CO₂ to actually end in a metastable liquid state rather than a stable one. Although, this scenario has not been tested, it nevertheless is possible. Finally, the work requirements calculated assumed that there was no change in potential energy of the material coming out of the adiabatic compressor. Depending on how the compressor is designed, this assumption is most likely an idealization and the actual work necessary will be slightly off from this paper's proposed value.

CO₂ is an excellent material for oil recovery. Its supercritical state has the potential to truly increase the efficiency and profitability of current oil recovery methods. CO₂ has been theoretically confirmed to have parameters ideal towards deep reservoir oil recovery, and the necessary parameters for conducting an experiment have been mapped out. The final step lies in placing supercritical CO₂ into action.

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