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Study of CO₂ Properties and Transportation for Injection well into Reservoir

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ABSTRACT

One of the possible solutions to reduce CO₂ emission in atmosphere is to inject for storage in reservoir. This action is known as the residual gas geological storage project. One of the important aspects in this project is the transportation of CO₂. CO₂ needs to be transported from the place where it is captured or extracted into reservoir. In this work, our concern is transportation from wellhead to reservoir.

When planning the CO₂ injection in an injection well, TOTAL MGR-team found that there is error about 15% in pressure profile calculated using oil and gas commercial software. This work is inspired by TOTAL experts in this area. The work done here is to expand understanding on CO₂ behavior when injected.

We start our work from finding CO₂ properties as the function of pressure and temperature from some correlations and methods. The accuracy of the results of each correlation/method is analyzed by comparing them and also with some other known software such as ALLPROPS and PVTSIM. The relative error from the comparison is then used as the indicator of selecting the “right” correlation/method to be used in pressure and temperature profile calculation.

This is followed by calculation of pressure and temperature profile along tubing for injection process. The work here is only limited to Adiabatic injection process (i.e. no heat in/out to/from the injection fluid) and one diameter straight vertical tubing. The flow condition studied are Steady State and Unsteady State/Transient flow. Hypothetical injection parameters are made as the base case for the analysis.

For Steady State flow, several scenarios such as: Static pressure, Isenthalpy process, Unisenthalpy-friction approach, and Unisenthalpy-constant internal energy are proposed and analyzed to get depth understanding of the injection process and its relation to the fluid properties and injection parameters. A cross check is also done with some commercial software (IPM-PROSPER and UNISIM). To observe the effect of injection

parameters to the behavior of pressure and temperature profiles along tubing, sensitivity analyses are investigated and the results are discussed and analyzed.

For unsteady state/transient period, we proposed some scenarios for special injection cases such as: Isothermal filling and Linearity approach. Those approaches are aim to give rough approximation of transient pressure and temperature along the pipe. However, it seems interesting to continue this work that explores different approaches.

All the calculations above are done with the help of programs made in MATLAB. Some examples of program code are given in appendix.

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1. SCOPE OF WORK

1.1 Contents of work

In this work, we consider only the issues below:

- Pure CO₂ fluid
- Adiabatic injection process
- One diameter straight vertical tubing/pipe

The main contents of this work are

- CO₂ properties as the function of pressure and temperature. The range of temperature and pressure are on what we called “area of interest” and near critical area (both of them are defined in fluid properties section)
- Comparisons between the values of CO₂ property (in the form of graphic) from every correlation/method that used to estimate the property and with ALLPROPS and PVTSIM. The analysis is made based on the comparison.
- Quantitative error analysis based on the comparisons of the CO₂ properties
- Pressure and Temperature profile from several scenarios of injection flow (detail will be explained on hydraulics section) for steady state and transient flow
- Sensitivity analysis of pressure and temperature profile along tubing
- Comparison with IPM-PROSPER and UNISIM
- Discussions and Conclusions

1.2 Methods of work

- Literature survey: Handbooks, Papers, Internet

Correlations and methods for CO₂ properties can be obtained from many sources such as handbooks, monograph, papers, internet, etc.

- Programming: MATLAB, Ms-Excel

After the correlations and methods are found, we can use it to calculate the fluid properties, say as the function of pressure and temperature. The program codes are needed to ease the tedious and complicated calculation. We used MATLAB program to do the calculation. Microsoft Excel is easy and convenient to be used for listing the data and plotting purpose.

- Comparison: ALLPROPS, PVTSIM, IPM-PROSPER, UNISIM

Result from some advanced commercial software is used as the comparison to result from program codes that we made, namely: ALLPROPS is the program to calculate the pure property of substance, PVTSIM is standard program in oil and gas industry to calculate the PVT properties for almost all components of oil and gas, IPM-PROSPER is the software to calculate the steady state pressure and temperature profile in the pipe, and UNISIM is the software for calculate any aspect related to equipments and processing.

- Analysis

Analysis is done based on the theory. Some important points are discussed more to get deeper understanding of it. If the deviation from theory presents, further observation, check, and test are done but if it is “persist”, the cause of it will be investigated if possible.

- Conclusions

From the whole analysis, the general conclusion can be taken. The conclusion has to be able to give reasonable and reliable explanations about the physic/phenomenon that occurs in injection flow.

2. BASIC THEORY AND CONCEPTS

2.1 INTRODUCTION

2.1.1 Carbon Dioxide

Carbon dioxide (CO₂) [28] is a slightly toxic, odorless, colorless gas with a slightly pungent, acid taste. Carbon dioxide is a small but important constituent of air. Its typical concentration is about 0.038% or 380 ppm. Exhaled air contains as much as 4% carbon dioxide.

Carbon dioxide is formed by combustion and biological processes including decomposition of organic material, fermentation and digestion. It combines with water in air to form carbonic acid which corrodes metals, limestone and marble. Large quantities are produced by lime kiln operation, ammonia production and magnesium production from dolomite.

The oceans hold much of the Earth's total inventory of CO₂ (the US National Oceanic and Atmospheric Administration estimates the oceans contain about 50 times more CO₂ than the atmosphere) however, neither air nor the oceans have concentrations great enough to make them commercially viable sources of carbon dioxide. Commercial quantities of carbon dioxide are produced by separating and purifying relatively CO₂-rich gases produced in combustion or biological processes that would otherwise be released directly to the atmosphere. Common sources are hydrogen plants, ammonia plants and fermentation operations such as production of beer or manufacture of ethanol from corn. CO₂ may also be recovered from underground formations in the western United States and in Canada.

Carbon dioxide will not burn or support combustion. Air with a carbon dioxide content of more than 10% will extinguish an open flame. Air containing more than 10% CO₂, if breathed, can be life-threatening. Such concentrations may build up in silos, digestion chambers, wells, sewers and the like.

CO₂ gas is 1.5 times as heavy as air, thus if released to the air it will concentrate at low elevations. Carbon dioxide will form "dry ice" at -78.5°C (-109.3° F). One kg of dry ice has the cooling capacity of 2 kg of ordinary ice. Gaseous or liquid carbon dioxide will form dry ice through an auto-refrigeration process if rapidly depressurized.

Carbon dioxide is commercially available as high pressure cylinder gas, relatively low pressure (about 300 psig or 20 barg) refrigerated liquid, or as dry ice. Large quantities are produced and consumed at industrial sites making fertilizers, plastics and rubber.

Carbon dioxide is a versatile material, being valued by various users for its reactivity, inertness and coldness. Common uses include fire extinguishing systems; carbonation of soft drinks; freezing of food products such as poultry, meats, vegetables and fruit; chilling of meats prior to grinding; refrigeration and maintenance of ideal atmospheric conditions during transportation of food products to market; enhancement of oil recovery from oil wells; raw material for production of various chemicals and treatment of alkaline water.

There is much interest and concern over the subject of global warming and its inter-relationship with levels of carbon dioxide in the air. Much of the rise in atmospheric CO₂ over the past 11,000 years, since the end of the last major glaciation period, pre-dates the industrial revolution and can be attributed to gradual warming of the oceans. The amount of CO₂ that the oceans can hold is temperature dependent, and post-glacial warming released a portion of the previously stored CO₂ to the atmosphere. Around 1800, at the end of the 300-years-long "Little Ice Age" period, and before the industrial revolution, the CO₂ level in the atmosphere was about 280 ppm, up from the immediate-post-glacial level of about 200 ppm. In 1960, the concentration of CO₂ in the atmosphere was 315 ppm. Since the mid-1900s, CO₂ levels have been increasing at an average annual rate in excess of 1 ppm, due to a combination of natural processes and increased combustion of fossil fuels. The average CO₂ concentration in the atmosphere is now about 380 ppm.

2.1.2 CO₂ Geological Storage Projects

As we know, the fossil fuels, i.e. oil and natural gas when being oxidized, would produce another gas which is the combination of carbon and oxygen as the result of oxidation. If the oxidation is done completely, the produced gas is named Carbon dioxide or simply by the symbol CO₂. Currently, the biggest producer of this gas is the industries. Oil and gas industry as the producer of fossil fuels also give the contribution on it. The excessive emission of CO₂ to atmosphere creates the issue of global warming due to the heat trapped in the atmosphere (green house effect). In order to reduce the emissions, one of the applicable methods is to inject the gas into the reservoir and keep it for long time. In oil industry, this kind of injection is also well known and applied as the secondary/tertiary recovery technique to improve oil and gas recovery (IOR/EOR).

Storage options for CO₂ in geological media can be divided into two primary categories and a secondary category [36]. The primary categories consist of

- Value added options - reservoirs that typically began as a commercially developed site to enhance recovery of fossil fuel fluids. However, they have a secondary benefit of providing a storage site for CO₂ (through the recovery process).
- Non-value added options – reservoirs that would only be developed to contain CO₂ emissions. Thus these are only economically viable if CO₂ emission reduction regulations were imposed or a revenue stream could be generated from sales of CO₂ credits. With the entry into force of the Kyoto Protocol 2005, non-value added options are currently attractive.

The secondary category is

- Industrial and natural analogues – a third category of geological CO₂ storage options exist that is done for other reasons than reducing CO₂ emissions. They have value but are either a natural phenomena or done for other economic reasons without any enhanced recovery of fossil fuels.

2.1.3 CO₂ injection well issues

The CO₂ storage begins with the capture of free CO₂ in the sources, purified until a certain level then transported into reservoir. We categorize the transportation into surface transportation and sub-surface transportation. Surface transportation usually uses pipeline where CO₂ is compressed and then being pumped through. Sub-surface transportation is CO₂ flow in the conduit (tubing/casing) into the bottom hole of the well. This work mainly focus on the flow in the well from surface until well bottom.

A good transportation design and planning is needed here to guarantee the safe and desired transportation. If the physic, behavior and any kind interaction of fluid with surrounding are known, the good design of transportation can be achieved. Here, CO₂ properties and thermodynamic related issues play important role in understanding the physic and behavior of fluid while being transported.

There are four issues connected with thermodynamic of acid gases (CO₂ is one of them) injected into reservoir [7]:

- Phase changes within the acid gas injector: The issue is to avoid phase changes between a liquid and gas, as they could create instabilities in the well operations.
- Water condensation: Condensation in the injectors is a risk as it could enhance internal corrosion. A proper model of this phenomenon could enable to implement the required dehydration of the gas without going to a complete dehydration.
- Pressure losses in the well: as a significant cost to any gas injection project is the compression capacity required to inject the gas, It is important to model pressure losses in the injectors.
- Down hole injection temperature: to model the flow and flow-rock interactions in the near well bore, It is necessary to model the down hole injection temperature, that will be dependant on Joule-Thomson effects in the well and heat exchange with the formations.

2.1.4 CO₂ Basic Constants

The following are the basic constant of CO₂ used in this work:

- Molecular weight : 44.01 gr/gr mole
- Triple point : -56.6 °C @ 5.173 bar
- Critical point : 31 °C (304.12 K) and 73.74 bar
- Density @ critical point : 464.73 kg/m³ (2.1518 cm³/gr)
- Accentric factor : 0.225
- Sublimization point (1 atm): -78.5 °C
- Compressibility factor z @ critical : 0.276
- Dipole momen : 0 debye
- Specific gravity @ 0 °C and 1 atm : 1.539 (1.9769 kg/m³)

2.1.5 Terminology used in this work

Area of Interest

The report for Well Injection Analysis for Rousse-1 [10] issued by MGR team of TOTAL, recommended that the surface injection temperature are above 40 °C which is above the critical temperature of CO₂ and the injection pressure ranging from 25 – 80 bara. Because this is an injection well, the pressure will increase due to the increase of the depth while the temperature depends on the heat transfer in/out the fluid within the well. Our model assumed adiabatic process which implies the temperature more likely to increase or at least will remain constant. It suggested that we observe more in this particular area of states:

$$\underline{40\text{ }^{\circ}\text{C} < T < 200\text{ }^{\circ}\text{C}} \text{ and } \underline{1\text{ bara} < P < 200\text{ bara}}$$

We call this specific area: Area of interest

Near Critical area

It is proved that the measurement of properties of fluid in the area near critical point is really difficult. Thus, the accuracy of property in this area is questionable. Again, It suggests that we should pay more attention to this near critical area:

$$\underline{25\text{ }^{\circ}\text{C} < T < 37\text{ }^{\circ}\text{C}} \text{ and } \underline{60 \text{ bara} < P < 86 \text{ bara}}$$

Percent error

This is the parameter to see how much the deviation of a value deviate from the reference value in the percentage form. The definition of percent error in this work is

$$e = 100x \frac{\text{value} - \text{reference_value}}{\text{reference_value}}$$

The reference value is the value which we trust more that the value is the real/true one. It can be obtained from experiments or other source that highly trusted by most of the people.

2.2 BASIC THEORY OF CO₂ PROPERTIES

2.2.1 CO₂ Phase Diagram

Figure below is CO₂ phase diagram (P-T plot).

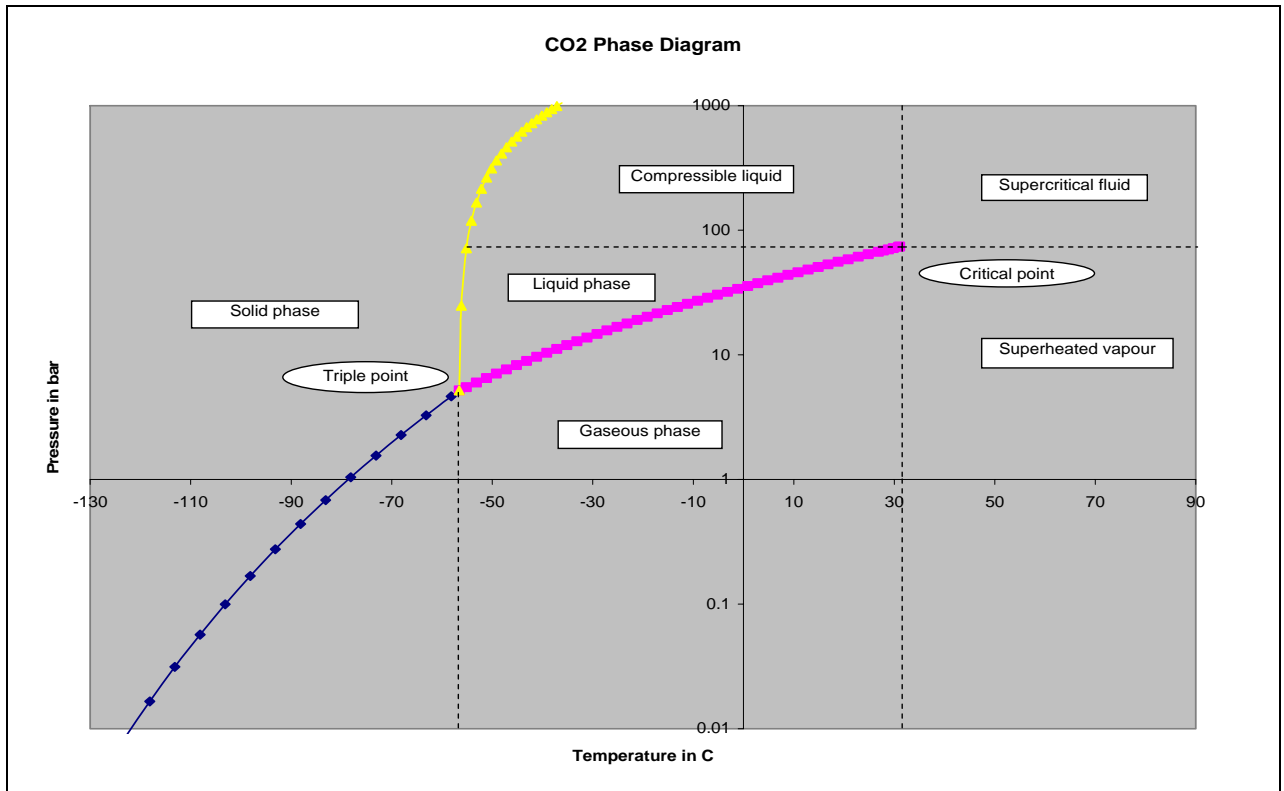


Fig. 2.1 CO₂ Phase Diagram (taken from Angus *et al.* [1])

The phase diagram shows the boundaries between each phase. The boundary between solid phase and gas phase is called sublimation line, solid phase and liquid phase is called melting line and liquid phase and gas phase is called saturation line. Each line contains two phases in equilibrium condition. The saturation line doesn't continue indefinitely. Instead, It terminates at a point called critical point.

For pure component, critical temperature is defined as the temperature where above of it, the gas can't be liquefied no matter how large the pressure is applied in it and vice versa

while critical pressure is defined as the pressure where beyond of it, the liquid can't be vaporized no matter how large the temperature we put on it and vice versa.

The difference between gas and liquid is molecules of liquid are dense, bond each other and not free to move while the gas are less dense, weaker bond and free to move. When the temperature of fluid is higher than its critical temperature, the molecules kinetic energy are so high. Thus the molecules are very active (superheated vapor). If we compact this fluid by putting the pressure on the fluid, the molecules can't move freely. If the pressure increase is maintained the molecules only being compacted but doesn't form the liquid bond. The density might look alike liquid but it's not liquid. This fluid is called supercritical fluid.

A big part of our area of interest is in superheated vapor and the small part in supercritical zone. This zone is the transition between fluid behaving like gas and fluid behaving like liquid.

One important issue in fluid injection is the phase change in the conduit. The main idea is to avoid the phase change because it can create instabilities in the well operation. In order to keep the phase unchanged, either we keep the temperature above the critical temperature or keep the pressure above the critical pressure. Both have their own disadvantages. To keep the pressure above its critical pressure, we need to compress the fluid and it could be very expensive while for the temperature, we can't fully control on it due to heat transfer occur along the conduit and could be unpredictable.

The phase change only happened exactly at the saturation points where a temperature has a unique saturation pressure or vice versa. The saturation points are obtained by experiment and can be reproduced by correlations. In this work, we use these correlations to find the saturation pressure as the function of temperature:

- Wagner correlation

$$P_{vpr} = \frac{P_{vp}}{P_c}, T_r = \frac{T}{T_c}$$

$$\ln P_{vpr} = \frac{a\tau + b\tau^2 + c\tau^3 + d\tau^4}{T_r}$$

where $\tau = 1 - T_r$

a = -6.95626, b = 1.19695, c = -3.12614, d = 2.99448, P_c = 73.8 bar and T = 304.15 K

- TOTAL correlation (valid for 216.58 – 304.21 K)

$$P^s(T) = \exp\left(A + \frac{B}{T} + C \ln T + DT^E\right)$$

A = 140.54, B = -4735, C = -21.268, D = 0.040909 and E = 1

P_s(T) is expressed in Pascal (Pa) and temperature in K.

In addition, we have some tabulation of the saturation values from Starling [20], Angus et al. [1], ALLPROPS, and from the reference [5].

What we do is we plot these saturation points from each correlation and from other sources, then compare and analyze the results.

2.2.2 CO₂ Density

Perhaps the most important property of the fluid for injection purpose is density. The density multiplies with gravity acceleration equal to pressure gradient. Pressure distribution can be estimated if the density is known. Density is defined as the mass of fluid per unit volume of fluid. Density can be also expressed as specific volume which is the volume of fluid per unit mass. So, density and specific volume are reciprocal. Liquid density is much higher than gas density which is vice versa for the specific volume. There are many methods to estimate the density of fluid, the popular one is known as Equation of State (EOS).

EOS relates pressure, temperature and specific volume. The simplest EOS is the ideal gas equation. Specific volume of fluid usually is expressed in mole base unit and we can always convert it into mass unit by the merit of molecular weight of the fluid. EOS is usually expressed explicitly in pressure instead of specific volume. Depends on the form of EOS, we can rearrange the equation such that it can be solved analytically for the specific volume (e.g. cubic equation of state in the form of third degree polynomial of specific volume). The EOS which can't be solved analytically is called non-analytical EOS. Examples for this kind of EOS are Benedict-Webb-Rubin EOS and its modifications.

In this work, we use following equation of state:

❖ Cubic Equation of State

- Peng-Robinson EOS (PR-EOS) [13]

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2}$$

$$b = \frac{0.07780RT_c}{P_c},$$

$$a = \frac{0.45724R^2T_c^2}{P_c} \left[1 + f\omega(1 - T_r^{1/2}) \right]^2$$

$$\text{where } f\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

- Soave-Redlich-Kwong EOS (SRK-EOS) [19]

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + bV}$$

$$b = \frac{0.08664RT_c}{P_c}$$

$$a = \frac{0.42748R^2T_c^2}{P_c} \left[1 + f\omega(1 - T_r^{1/2}) \right]^2$$

$$\text{where } f\omega = 0.48 + 1.574\omega - 0.176\omega^2$$

- Patel-Teja EOS (PT-EOS) [12]

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + c(V - b)}$$

$$a = \Omega_a \frac{R^2T_c^2}{P_c} \alpha(T_r)$$

$$b = \Omega_b \frac{RT_c}{P_c}$$

$$c = \Omega_c \frac{RT_c}{P_c}$$

where

$$\Omega_c = 1 - 3\zeta_c$$

$$\Omega_a = 3\zeta_c^2 + 3(1 - 2\zeta_c)\Omega_b + \Omega_b^2 + 1 - 3\zeta_c$$

and Ω_b is the smallest positive root of the cubic equation:

$$\Omega_b^3 + (2 - 3\zeta_c)\Omega_b^2 + 3\zeta_c^2\Omega_b - \zeta_c^3 = 0$$

$$\alpha(T_r) = \left(1 + F(1 - \sqrt{T_r})\right)^2$$

The generalized parameters:

$$F = 0.452413 + 1.30982\omega - 0.295937\omega^2$$

$$\zeta_c = 0.329032 - 0.076799\omega + 0.0211947\omega^2$$

- Twu EOS (Modification of PR-EOS) [16]

It is mainly the same with PR-EOS, the only difference is on the right hand side of a term.

$$a = \frac{0.45724R^2T_c^2}{P_c} \left[T_r^{-0.171813} \exp(0.125283(1 - T_r^{1.77634})) + \omega \left(\frac{T_r^{-0.607352} \exp(0.511614(1 - T_r^{2.20517}))}{T_r^{-0.171813} \exp(0.125283(1 - T_r^{1.77634}))} - 1 \right) \right]$$

- Trebble-Bishnoi EOS (four parameter cubic EOS) [21]

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + (b + c)V - (bc + d^2)}$$

$$(T_c P_c)_H = 1876 - 1160\omega$$

$$Z_c = 0.29 - 0.0885\omega - 0.0005(\sqrt{T_c P_c} - \sqrt{(T_c P_c)_H})$$

$$q_1 = 0.35 + 0.7924\omega + 0.1875\omega^2 - 28.93(0.3 - Z_c)^2$$

$$q_2 = 0.05246 + 1.15058\omega - 1.99348\omega^2 + 1.5949\omega^3 - 1.39267\omega^4$$

$$\zeta_c = 1.075Z_c$$

$$Cc = 1 - 3\zeta_c$$

$$c = Cc \frac{RT_c}{P_c}$$

$$d = 0.341V_c - 0.005$$

$$Dc = d \frac{P_c}{RT_c}$$

V_c is in dm³/mol or m³/kmol.

Bc is the smallest positive root of the equation:

$$Bc^3 + (2 - 3\zeta_c)Bc^2 + 3\zeta_c^2 Bc - (Dc^2 + \zeta_c^3) = 0$$

$$Ac = (3\zeta_c^2 + 2BcCc + Bc + Cc + Bc^2 + Dc^2) \frac{R^2 T_c^2}{P_c}$$

$$\alpha = \exp(q1(1 - T_r))$$

$$a = \alpha Ac$$

$$\beta = 1 + q2(1 - T_r + \ln(T_r)) \quad \text{if } T_r \leq 1 \text{ and if } T_r > 1, \text{ then}$$

$$\beta = 1$$

$$b = \beta Bc \frac{RT_c}{P_c}$$

❖ Non-Analytical Equation of State

- Starling-Benedict-Webb-Rubin (SBWR, eleven parameter EOS) [20]

$$P = \rho RT + (B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4}) \rho^2 + (bRT - a - \frac{d}{T}) \rho^3 +$$

$$\alpha(a + \frac{d}{T}) \rho^6 + \frac{c\rho^3}{T^2} (1 + \gamma\rho^2) \exp(-\gamma\rho^2)$$

where $A_0 = 6592.03$, $B_0 = 0.394117$, $C_0 = 295902 \times 10^4$, $D_0 = 409151 \times 10^6$, $E_0 = 102898 \times 10^5$, $a = 5632.85$, $b = 0.971443$, $c = 274668 \times 10^4$, $d = 59929.7$, $\alpha = 0.395525$, and $\gamma = 1.64916$

The units for these parameters correspond to pressure in psia, temperature in ⁰R, and molar density in lb.-mole/cu. ft. These parameter values were determined using 44.011 for the molecular weight of carbon dioxide and $R = 10.7335$ for the gas constant.

The SBWR-EOS is in the form of pressure explicitly as the function of the temperature and density instead of specific volume. It is difficult if not impossible to solve this equation analytically for the density as the function of pressure and temperature. Numerical way to solve it is using trial and error method. The suggested algorithm [20] is to calculate the pressure using incremental step of density until the calculated pressure is within error tolerance (limiting value where the difference still can be excepted). For gas

we can use incremental of 0.01 lb.mole/cu.ft. and initial estimate of 0 then calculated upward/increases while for liquid, we can use incremental of 0.05 with initial estimate of 2.5 then calculated downward/decreases.

At saturation points, there are two density namely liquid and gas density. These densities can be obtained analytical directly from the cubic equation of state with putting input of the set of saturation pressure and temperature. The number of positive roots of cubic EOS is either 1 or 3. In case of only one root, the value is the value of specific volume but in other case, only the smallest root and the largest root are taken as the value of specific volume (i.e. the smallest is liquid and the largest is gas). Then, the density is reciprocal of specific volume.

Special for the saturated liquid density, TOTAL [7] has recommended this correlation:

$$\rho = \frac{A}{B^{(1+(1-T/C)^p)}}$$

ρ is expressed in kmol/m³ and T is in Kelvin. It is valid for the range of temperature 216.58 – 304.21 K

The plots of density can be made based on each EOS above and from the correlation. The results are analyzed to get understanding how the density behavior as the pressure and/or temperature changed.

2.2.3 CO₂ Viscosity

Viscosity is a measure of the resistance of the substance to deform under shear stress. Viscosity describes a fluid's internal resistance to flow. The high value of viscosity means the substance has high resistance thus it is "difficult" to flow. All real fluids have some resistance to shear stress (except for superfluids/ideal fluid). The viscosity is defined as

$$\tau = \eta \frac{\partial u}{\partial y}$$

τ is shear stress, $\frac{\partial u}{\partial y}$ is velocity gradient/ the rate of shear deformation, and η is a constant known as the coefficient of viscosity or simply viscosity.

It is obvious that the relation between shear stress and shear rate is linear since the viscosity is constant. Many fluids, such as water and most of gases, satisfy this relationship and are known as Newtonian fluids. Non-Newtonian fluids exhibit a more complicated relationship between shear stress and velocity gradient than simple linearity.

There are two mechanisms which explain the viscosity behavior of fluids. The first is the momentum transports between the molecule layers and the second is the cohesion forces of between molecules. The cohesion force of molecules in gas phase is relatively smaller than liquid phase. Thus, the first mechanism is dominant. When the temperature of the fluid increase, the momentum transports between molecules increase as well and give the effect of the increase of internal resistance to flow (i.e. the viscosity increase). For liquid, the reversal mechanism applied where the increase of temperature weakening the molecules cohesion force which give effect of the decrease in flow resistance.

Viscosity may be thought of as the measure of fluid friction. Viscosity is needed to calculate Reynold's number which is one of the parameter to calculate the friction force. Therefore viscosity is also one of the important properties (after density) of fluid in sense

of pressure distribution estimation of the fluid flow. Together with thermal conductivity, we categorized both as the transport properties of fluid.

The CO₂ viscosity can be estimated using many viscosity correlations but in this work where we concern on the specific area called **area of interest**, a combine correlation is suggested to use to estimate the viscosity in this area namely Chung et al. method to calculate the low pressure viscosity and Reichenberg correlation to add the effect of pressure. So, in order to estimate the viscosity as the function of pressure and temperature, low pressure viscosity which is function of temperature only need to be calculated. Afterward the pressure effect is then added using “pressure effect correlation” to get the viscosity value.

- Chung et al. correlation to estimate low pressure viscosity [4]

$$T_r = \frac{T}{T_c}$$

$$T^* = 1.2593T_r$$

$$\zeta = 1.16145(T^*)^{-0.14874} + 0.52487 \exp(-0.7732T^*) + 2.16178 \exp(-2.43787T^*)$$

$$\eta_0 = 12.23415053 \frac{T^{0.5}}{\zeta}$$

Temperature is in Kelvin and η_0 is in mikroPoise.

- Reichenberg method to add the effect of pressure [17]

$$\alpha_1 = 0.0019824, \alpha_2 = 5.2683, a = -0.5767, \beta_1 = 1.6552, \beta_2 = 1.276, \gamma_1 = 0.1319,$$

$$\gamma_2 = 3.7035, c = -79.8678, \Delta_1 = 2.9496, \Delta_2 = 2.919, d = -16.6169$$

$$A = \frac{\alpha_1}{T_r} \exp(\alpha_2 T_r^a)$$

$$B = A(\beta_1 T_r - \beta_2)$$

$$C = \frac{\gamma_1}{T_r} \exp(\gamma_2 T_r^c)$$

$$D = \frac{\Delta_1}{T_r} \exp(\Delta_2 T_r^d)$$

$$P_r = \frac{P}{P_c}$$

$$r = 1 + \left(\frac{AP_r^{1.5}}{BP_r + (1 + CP_r^D)^{-1}} \right)$$

The viscosity as the function of pressure and temperature in mikroPoise is

$$\eta = \eta_0 r$$

Vesovic et al. (1990) [26] give an extensive, fine quality review on the transportation properties of the carbon dioxide. One of these properties is the viscosity. The result from Vesovic's work is taken as the reference for the transport properties in this work. We also add one more source as the comparison material to the correlation suggested above: PVTsim (Commercial PVT software commonly used in Petroleum industry).

TOTAL recommended these correlations to estimate the viscosity of saturated gas and the viscosity of saturated liquid:

- Viscosity of saturated liquid (valid for 216.58 – 303.15 K) [7]

$$\mu^L = \exp\left(A + \frac{B}{T} + C \ln T + DT^E\right)$$

where A = 18.775, B = -402.92, C = -4.6854, D = -6.9171 x 10⁻²⁶, and E = 10

μ^L is expressed in Pa.s and T in Kelvin.

- Viscosity of saturated gas (valid for 194.67 – 1500 K) [7]

$$\mu^v = \frac{AT^B}{1 + \frac{C}{T} + \frac{D}{T^2}}$$

where A = 2.1480 x 10⁻⁶, B = 0.46, C = 290, D = 0

μ^v is expressed in Pa.s and T in Kelvin.

2.2.4 CO₂ Internal Energy

Internal energy (U) of a thermodynamic system or a body with well-defined boundaries is the total kinetic energy due to the motion of molecules (translational, rotational, vibrational) and the potential energy associated with the vibrational and electric energy of atoms within molecules or crystals. It includes the energy in all the chemical bonds and the energy of the free, conduction electrons in metals. Internal energy does not include the translational or rotational kinetic energy of a body as a whole. It excludes any potential energy a body may have because of its location in external gravitational or electrostatic field.

The internal energy is essentially defined by the first law of thermodynamic which states that the energy is conserved [3]:

$$\Delta U = Q - W$$

where

ΔU is the change in internal energy of a system during a process.

Q is heat added to a system; positive value for heat flow into a system while negative value for the heat flow out of a system.

W is mechanical work done by a system

The equation above can be re-written in infinitesimal form as:

$$dU = \delta Q - \delta W$$

The d before the internal energy function indicates that it is an exact differential. In other words it is a state function or a value which can be assigned to the system. On the other hand, the δ 's before the q and w terms indicate that they describe increments of energy which are not state functions but rather they are processes by which the internal energy is changed.

The internal energy may be expressed in terms of other thermodynamic parameters. Each term is composed of an intensive variable (a generalized force) and its conjugate infinitesimal extensive variable.

Assume the work and heat interchange reversibly, the work done by the system may be related to the pressure and volume as:

$$\delta W = PdV$$

And the heat can be related to the temperature and entropy based on the second law of thermodynamic:

$$\delta Q = TdS$$

Using the above equations to construct one possible expression for the internal energy gives:

$$dU = TdS - PdV$$

This simply says that the change of internal energy of the system is contributed by the entropy change of the system and the change of system volume.

The internal energy cannot precisely be measured. This is because only changes in the internal energy can be measured, and the total internal energy of a given system is the difference between the internal energy of the system and the internal energy of the same system at absolute zero temperature. Since absolute zero cannot be obtained, the total internal energy cannot be precisely measured. The same is true of other thermodynamic parameters such as enthalpy and entropy.

One of the methods to estimate the value of internal energy is using so called departure function/residual function. By mathematic manipulation, the difference of internal energy between two states can be written as:

$$u_2 - u_1 = (u_1^* - u_1) - (u_2^* - u_2) + (u_2^* - u_1^*)$$

The “star superscript” sign refers to **ideal gas** condition. 1 and 2 subscript signs refer to two different states. The first and second term in right hand side of equation is known as internal energy departure/residual function. A departure function is defined as the

difference between the property as computed for an ideal gas and the property of the real gas for a specified temperature T and pressure P. Common departure functions include those for enthalpy, entropy and internal energy. The third term is the difference of internal energy between two states under ideal gas and it is possible to calculate it using the ideal gas equation.

Departure function for internal energy under certain P and T can be obtained by this relation:

$$(u^* - u) = (h^* - h) - P(v^* - v)$$

In order to get departure function for internal energy, the departure function of enthalpy has to be obtained first (Enthalpy departure function will be discussed in the next sub-chapter) and two equation of state are needed namely one real gas EOS and another is ideal gas equation, to calculate the real gas specific volume and ideal gas specific volume respectively.

Internal energy difference between two states under ideal condition can be written as:

$$u_2^* - u_1^* = (h_2^* - h_1^*) - (P_2 v_2^* - P_1 v_1^*)$$

The first term in right hand side of equation is the difference of enthalpy between two states under ideal condition. It can be calculated theoretically using ideal gas specific heat and will be the subject of the discussion in enthalpy section.

If we arbitrarily take one state P, T as the reference value in internal energy difference calculation, we get “absolute value” for every P, T. This absolute value for the same P, T may differ depend on the datum used but the difference between two states have to be the same. Usually the temperature of zero and the pressure of zero or ambient pressure are taken as the reference but this is not necessary as long as we consistently use the same datum for whole system. In this work, we use the reference point of **300 K and 1 bar**.

In this work, we use three equations of state to estimate the value of internal energy, enthalpy and entropy of CO₂ as the function of pressure and temperature:

- Peng-Robinson EOS
- Soave-Redlich-Kwong EOS
- Starling-Benedict-Webb-Rubin EOS

The results are compared with the reference which is taken from the work of Angus et al. [1] for internal energy and enthalpy. We use ALLPROPS as the reference for entropy.

2.2.5 CO₂ Enthalpy

This term refers to enthalpy change of formation. Enthalpy (often called heat content) is a quotient or description of thermodynamic potential of a system. It is defined as

$$H = U + PV$$

where H is the enthalpy, U is the internal energy, P is the pressure of the system, and V is the volume. The term PV is known as flow work.

The same way with internal energy estimation is imposed to estimate the value of enthalpy as function of pressure and temperature.

$$h_2 - h_1 = (h_1^* - h_1) - (h_2^* - h_2) + (h_2^* - h_1^*)$$

Thus we need the enthalpy departure function and the difference of enthalpy between two states under ideal condition. Enthalpy departure function can be obtained using this relation:

$$h^* - h = (f^* - f) + T(s^* - s) + P(v^* - v)$$

$(f^* - f)$ is Helmholtz energy departure function. We can get this value if we have an equation of state for real gas and an ideal gas equation due to relations:

$$v^* = \frac{RT}{P}$$

$$f^* - f = \int_{\infty}^v \left[P(v, T) - \frac{RT}{v} \right] dv + RT \ln \frac{v}{v^*}$$

$(s^* - s)$ is entropy departure function and can be obtained using the following equation:

$$s^* - s = - \left(\frac{\partial(f^* - f)}{\partial T} \right)_v$$

Entropy departure function from some equation of state will be discussed in the next sub-chapter.

The following are the enthalpy departure function from some equation of state:

- Peng-Robinson EOS enthalpy departure function

$$h^* - h = -RT_c \left[T_r(z-1) - 2.078(1+\kappa)\sqrt{\alpha} \ln \left(\frac{z+2.414B}{z-0.414B} \right) \right]$$

where

$$\alpha = [1 + f\omega(1 - T_r^{1/2})]^2$$

$$T_r = \frac{T}{T_c}$$

$$P_r = \frac{P}{P_c}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$B = 0.0778 \frac{P_r}{T_r}$$

$$z = \frac{v}{v^*}$$

T_c is critical temperature, P_c is critical pressure, z is compressibility factor, and ω is acentric factor [13].

- Soave-Redlich-Kwong EOS enthalpy departure function

$$h^* - h = \left(a + f\omega \sqrt{\frac{a_c a T}{T_c}} \right) \frac{1}{b} \ln \frac{v+b}{v} + P(v^* - v)$$

where

$$a_c = \frac{0.42748R^2 T_c^2}{P_c}$$

a, b, $f\omega$, T_c and P_c are as defined in the Soave-Redlich-Kwong equation of state [19].

- Starling-Benedict-Webb-Rubin EOS enthalpy departure function

$$\Phi(h^* - h) = - \left(B_0 RT - 2A_0 - \frac{4C_0}{T^2} + \frac{5D_0}{T^3} - \frac{6E_0}{T^4} \right) \rho - \frac{1}{2} \left(2bRT - 3a - \frac{4d}{T} \right) \rho^2 - \frac{1}{5} \alpha \left(6a + \frac{7d}{T} \right) \rho^5 - \frac{c}{\gamma T^2} \left[3 - \left(3 + \frac{1}{2} \gamma \rho^2 - \gamma^2 \rho^4 \right) \exp(-\gamma \rho^2) \right]$$

Φ is conversion factor from Btu/lb to psia cu. ft./lb-mole. The others coefficient are as defined in SBWR-EOS [20].

The difference of enthalpy between two states under ideal condition can be estimated using this equation:

$$h_2^* - h_1^* = \int_{T_1}^{T_2} c_p^*(T) dT$$

$c_p^*(T)$ is ideal gas specific heat/heat capacity at constant pressure.

In order to solve the integral for T we need the expression for $c_p^*(T)$ as the function of temperature. Reid, Prausnitz and Poling [15] suggested to use a third degree polynomial to express it:

$$c_p^*(T) = a + bT + cT^2 + dT^3$$

They also present tabular values for the parameters a, b, c and d for over 600 different components. For CO₂, the constants are $a = 19.8$, $b = 7.344 \times 10^{-2}$, $c = -5.602 \times 10^{-5}$, $d = 1.715 \times 10^{-8}$.

Now, all terms to calculate the difference of enthalpy between two states are known, so the enthalpy as the function of pressure and temperature can be calculated. The internal energy departure function can now be derived and the difference of internal energy between two states can be calculated.

2.2.6 CO₂ Entropy

Entropy is an extensive state function that accounts for the effects of irreversibility in thermodynamic systems. This concept is central in second law of thermodynamics, which deals with physical processes and whether they occur spontaneously. Spontaneous changes occur with an increase in entropy. Spontaneous changes tend to smooth out differences in temperature, pressure, density, and chemical potential that may exist in a system, and entropy is thus a measure of how far this smoothing-out process has progressed. Recently, entropy has been interpreted in terms of the “dispersal” of energy.

When a system’s energy is defined as the sum of its “useful” energy, and its “useless energy”, then entropy may be (most concretely) visualized as the “scrap” or “useless” energy whose energetic prevalence over the total energy of a system is directly proportional to the absolute temperature of the considered system. The change of entropy when multiplied by a reference temperature, can be understood as a measure of the amount of energy in a physical system that cannot be used to do thermodynamic work.

More precisely, in any process where the system gives up energy ΔE , and its entropy falls by ΔS , a quantity at least $T_R \Delta S$ of that energy must be given up to the system’s surroundings as unusable heat (T_R is the temperature of the system’s external surroundings). Otherwise the process will not go forward. The second law of thermodynamics: “The algebraic sum of all the transformations occurring in cyclical process can only be positive, or, as an extreme case, equal to nothing” or in mathematical expression:

$$\int \frac{\partial Q}{T} \geq 0$$

Entropy of the fluid can be estimated using the same method for finding internal energy and enthalpy which is using departure function method. The difference of entropy between two states is calculated using equation:

$$s_2 - s_1 = (s_1^* - s_1) - (s_2^* - s_2) + (s_2^* - s_1^*)$$

The first and second terms in right hand side of equation are entropy departure function for each state and the most right term is the difference of entropy between two states under ideal condition.

Recall the equations for finding the entropy departure function:

$$s^* - s = - \left(\frac{\partial(f^* - f)}{\partial T} \right)_v$$

where Helmholtz energy departure function is defined as [3]

$$f^* - f = \int_{\infty}^v \left[P(v, T) - \frac{RT}{v} \right] dv + RT \ln \frac{v}{v^*}$$

Equation of state for real gas and ideal gas are needed to obtain entropy departure function. The following are the entropy departure function from some of EOS:

- Peng-Robinson EOS entropy departure function

$$s^* - s = -R \left[\ln(z - B) - 2.078\kappa \left(\frac{1 + \kappa}{\sqrt{T_r}} - \kappa \right) \ln \left(\frac{z + 2.414B}{z - 0.414B} \right) \right]$$

where

z , B , T_r , and κ are as defined in PR-EOS enthalpy departure function.

- Soave-Redlich-Kwong EOS entropy departure function

$$s^* - s = -R \ln \frac{v-b}{v^*} + \frac{f\omega}{b} \sqrt{\frac{a_c a}{TT_c}} \ln \frac{v+b}{v}$$

a, a_c, b, fω, T_c and P_c are as defined in the Soave-Redlich-Kwong equation of state.

- Starling-Benedict-Webb-Rubin EOS entropy departure function

$$\phi(s^* - s) = R \ln(\rho RT) + \left(B_0 R + \frac{2C_0}{T^3} - \frac{3D_0}{T^4} + \frac{4E_0}{T^5} \right) \rho + \frac{1}{2} \left(bR + \frac{d}{T^2} \right) \rho^2 - \frac{\alpha d \rho^5}{5T^2} - \frac{2c}{\gamma T^3} \left[1 - \left(1 + \frac{1}{2} \gamma \rho^2 \right) \exp(-\gamma \rho^2) \right]$$

Φ is conversion factor from Btu/lb to psia cu. ft./lb-mole. The others coefficient are as defined in SBWR-EOS.

The difference of entropy between two states under ideal condition can be calculated using this equation:

$$s_2^* - s_1^* = \int_{T_1}^{T_2} \frac{c_p^*(T)}{T} dT + R \ln \frac{P_1}{P_2}$$

$c_p^*(T)$ is ideal gas constant pressure specific heat/heat capacity and can be calculated using many correlations. One of them is the correlation written on sub-chapter CO₂ enthalpy.

2.2.7 CO₂ Heat Capacity/Specific heat

Heat capacity is a measurable physical quantity that characterizes the ability of a body to store heat as it changes in temperature. Heat capacity is an “extensive quantity” because it is sensitive to the size of the object while specific heat (i.e. heat capacity divided by body mass) is an “intensive quantity”. Here, we will only discuss molar specific heat as the function of pressure and temperature.

Molar specific heat is defined as the rate of change of temperature as heat is added to a body at given conditions and state of the body (foremost its temperature) per mole of fluid. There are two kinds of specific heat: constant pressure specific heat and constant volume specific heat.

Mathematical expression of the definition of both specific heats is

$$C_p = \left(\frac{\delta Q}{dT} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

$$C_v = \left(\frac{\delta Q}{dT} \right)_v = \left(\frac{\partial U}{\partial T} \right)_v = T \left(\frac{\partial S}{\partial T} \right)_v$$

Both of the specific heat is related each other by this relation:

$$C_p = C_v - T \frac{\left(\frac{\partial P}{\partial T} \right)_v^2}{\left(\frac{\partial P}{\partial v} \right)_T}$$

For ideal gas, the equation above simplified to

$$C_p = C_v + R$$

The constant pressure specific heat for real fluid can be calculated using the following equation:

$$C_p = C_p^*(T) - R - T \int_v^\infty \left[\left(\frac{\partial^2 P}{\partial T^2} \right)_v \right] dv - T \frac{\left(\frac{\partial P}{\partial T} \right)_v^2}{\left(\frac{\partial P}{\partial v} \right)_T}$$

$C_p^*(T)$ is ideal gas specific heat (the same as in enthalpy/entropy departure function on ideal condition). The rest of terms can only be solved if we have equation of state.

These are the expression for the terms needed to calculate specific heat derived from some equations of state:

- Peng-Robinson EOS specific heat terms

$$\frac{da}{dT} = -a_c \frac{f\omega}{\sqrt{TT_c}} (1 + f\omega(1 - \sqrt{T_r}))$$

$$\left(\frac{\partial P}{\partial v} \right)_T = \frac{-RT}{(v-b)^2} + \frac{2a(v+b)}{(v^2 + 2bv - b^2)}$$

$$\left(\frac{\partial P}{\partial T} \right)_v = \frac{R}{(v-b)} - \frac{\left(\frac{da}{dT} \right)}{(v^2 + 2bv - b^2)^2}$$

$$\int_v^\infty \left[\left(\frac{\partial^2 P}{\partial T^2} \right)_v \right] dv = \frac{0.17678}{abT} \left(\frac{da}{dT} \right) \left(T \left(\frac{da}{dT} \right) - a \right) \ln \left(\frac{v + 2.414b}{v - 0.414b} \right)$$

- Soave-Redlich-Kwong EOS specific heat terms

$$\frac{da}{dT} = -a_c \frac{f\omega}{\sqrt{TT_c}} \left(1 - f\omega(1 - \sqrt{T_r})\right)$$

$$\left(\frac{\partial P}{\partial v}\right)_T = \frac{-RT}{(v-b)^2} + \frac{a(2v+b)}{(v^2+bv)^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{(v-b)} - \frac{\left(\frac{da}{dT}\right)}{(v^2+bv)}$$

$$\int_v^\infty \left[\left(\frac{\partial^2 P}{\partial T^2}\right)_v\right]_T dv = \frac{0.5f\omega}{abT} \sqrt{\frac{a_c a}{TT_c}} \left(T \left(\frac{da}{dT}\right) - a\right) \ln\left(\frac{v+b}{v}\right)$$

- Starling-Benedict-Webb-Rubin EOS specific heat terms

$$\left(\frac{\partial P}{\partial T}\right)_v = R\rho + \left(B_0R + \frac{2C_0}{T^3} - \frac{3D_0}{T^4} + \frac{4E_0}{T^5}\right)\rho^2 + \left(bR + \frac{d}{T^2}\right)\rho^3 - \frac{\alpha d}{T^2}\rho^6 - \frac{2c}{\rho^3 T^3} (1 + \gamma\rho^2) \exp(-\gamma\rho^2)$$

$$\left(\frac{\partial P}{\partial v}\right)_T = -RT\rho^2 - 2\left(B_0RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4}\right)\rho^3 - 3\left(bRT - a - \frac{d}{T}\right)\rho^4 - 6\alpha\left(a + \frac{d}{T}\right)\rho^7 + \frac{c}{T^2} \\ (-3\rho^4 - 3\gamma\rho^6 + 2\gamma^2\rho^8) \exp(-\gamma\rho^2)$$

$$\int_v^\infty \left[\left(\frac{\partial^2 P}{\partial T^2}\right)_v\right]_T dv = \left(\frac{-6C_0}{T^4} + \frac{12D_0}{T^5} - \frac{20E_0}{T^6}\right)\rho - \frac{d}{T^3}\rho^2 + \frac{2\alpha d}{5T^3}\rho^5 + \frac{6c}{\gamma T^4} \left(1 - \left(1 + \frac{1}{2}\gamma\rho^2\right) \exp(-\gamma\rho^2)\right)$$

All coefficients refer to its original equation of state. After all terms are known, we can first calculate the constant pressure specific heat then calculate the constant volume specific heat as the function of pressure and temperature only.

C_p and C_v are calculated from three EOS above and compared with the reference which is Angus et al [1]. The results are analyzed to get better understanding of specific heat behavior.

2.2.8 CO₂ Joule-Thomson (JT) coefficient

Joule-Thomson effect is a process in which the temperature of a real gas is either decreased or increased by letting the gas expand freely at constant enthalpy (i.e. no heat is transferred to or from the gas, and no external work is extracted). When volume is increased in an irreversible process, the gas laws do not uniquely determine what happens to the pressure and temperature of the gas. Isentropic expansion, in which the gas does positive work in the process of expansion, always causes a decrease in temperature.

When a real gas expands freely at constant enthalpy, the temperature may either decrease or increase, depending on the initial temperature and pressure. For any given pressure, a real gas has a Joule-Thomson inversion temperature, above which expansion at constant enthalpy causes the temperature to rise, and below which expansion at constant enthalpy causes cooling. For most of gases at atmospheric pressure, the inversion temperature is fairly high (above room temperature), and so most gases at those temperature and pressure conditions are cooled by isenthalpic expansion.

There are two mechanisms which explain the decrease or increase of temperature when expanded at constant enthalpy. The first, as the gas expands, the average distance between molecules grows. Because of intermolecular attractive forces, expansion causes an increase in the potential energy of the gas. If no external work is extracted in the process (“free expansion”) and no heat is transferred in or out the gas, the total energy of the gas remains the same because of the conservation of energy (i.e. constant enthalpy) then the increase in potential energy thus means the decrease in kinetic energy and therefore in temperature.

The second mechanism has the opposite effect. During gas molecule collisions, kinetic energy is temporarily converted into potential energy. As the average intermolecular

distance increases, there is a drop in the number of collisions per time unit, which causes a decrease in average potential energy. Again, total energy is conserved, so leads to an increase in kinetic energy (temperature). The decrease or increase of temperature is determined by which of mechanism effect dominates at the state of gas before expansion

The Joule-Thomson coefficient is defined as the change of temperature with respect to a change of pressure in a Joule-Thomson process. In mathematical expression:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

The value of μ_{JT} depends on the specific gas, pressure and temperature of gas before expansion. When it is equal to zero at some state called the inversion state and the Joule-Thomson inversion temperature is the temperature where the coefficient changes sign. The negative value of μ_{JT} means the isenthalpic expansion causes the decrease of the gas temperature while the positive value of μ_{JT} means the isenthalpic expansion causes the gas temperature to increase.

The value of μ_{JT} for ideal gases is always equal to zero. Thus they will neither heat nor cool upon being expanded at constant enthalpy. The real gas at very low pressure (approaches ideal behavior) shows that the temperature almost neither increase nor decrease when being expanded at constant enthalpy.

Joule-Thomson coefficient is important property to estimate the final temperature of expanded gas. If we know the change of pressure then the change of temperature can be estimated. This is important when we want to calculate the pressure and temperature distribution of the gas flow in the conduit. The estimate from Joule-Thomson coefficient makes the calculation of pressure and temperature much easier and faster.

Joule-Thomson coefficient as the function of pressure and temperature can be calculated using this equation:

$$\left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{C_p} \left(T \left(\frac{\partial v}{\partial T}\right)_P - v \right)$$

Obviously that to get the value of Joule-Thomson coefficient, the constant pressure specific heat has to be obtained first then an equation of state is needed to calculate the derivative of specific volume with respect to temperature at constant pressure. It depends on equation of state but usually most of equation of state's are implicit on specific volume which causes the difficulty to get the derivative of specific volume with respect to temperature at constant pressure. However, by a little mathematical manipulation, this term can be re-written as:

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{\left(\frac{\partial P}{\partial T}\right)_v}{\left(\frac{\partial P}{\partial v}\right)_T}$$

Numerator and denominator term for PR-EOS, SRK-EOS, and SBWR-EOS has been derived and can be viewed in the previous sub-chapter (CO₂ specific heat). Now, we can get the value of Joule-Thomson coefficient as the function of pressure and temperature. As usual, the results are compared and analyzed. The reference for this property is taken from Peng-Robinson EOS due to the lack of other sources for this property.

2.2.9 CO₂ Thermal Conductivity

Thermal conductivity, k (or sometime λ), is the intensive property of a material that indicates its ability to conduct heat. It is defined as the proportion factor in equation:

$$\frac{\delta \dot{Q}}{dA} = k \frac{dT}{dx}$$

where \dot{Q} is heat flow rate, A is area of heat transfer, T is temperature, x is the distance of heat being transferred and k is thermal conductivity. The equation simply says that the flux of heat is proportional to temperature gradient.

Heat can be transferred by three ways: conduction, convection and radiation. For the application of estimation of temperature distribution of the fluid flow in the conduit with heat transfer phenomenon which heat is transferred in/out from the fluid from/to surroundings, conduction plays dominant role in the process. All thermal conductivity from material involved in heat transfer processes have to be known in order to calculate the overall heat transfer coefficient which relates the heat and temperature of the media where the heat pass through. This is a reason why thermal conductivity of the fluid is important to be obtained.

A detail observation of the fluid flow through the conduit (e.g. the pipe), show that in area near the wall, there is a very thin layer where the heat is transferred by conduction. This layer determined what would the temperature of the fluid inside the pipe. When its conductivity is low, the difference of temperature between the wall and the core of fluid would be very large while it is high, the difference is small. The fluid core itself, which

for the case of turbulence, the temperature of fluid almost constant. Thus it can be assumed homogeneous due to effective mixing of fluid (convective heat transfer).

Here we provide one method to find the thermal conductivity of CO₂ in the **area of interest** namely Chung et al. method [4]:

$$F_c = 1 - 0.275\omega$$

$$T^* = 1.2593T_r$$

$$\zeta = AT^{*-B} + C \exp(-DT^*) + E \exp(-FT^*)$$

$$\vartheta = 10^{-7} \left(40.785 F_c \frac{MT^{0.5}}{V_c^{2/3} \zeta} \right)$$

$$\alpha = \frac{C_v^*}{R} - 1.5$$

$$\beta = 0.7862 - 0.7109\omega + 1.3168\omega^2$$

$$Z = 2 + 10.5T_r^2$$

$$\psi = 1 + \alpha \left(\frac{0.215 + 0.28288\alpha - 1.061\beta + 0.26665Z}{0.6366 + \beta Z + 1.061\alpha\beta} \right)$$

$$\lambda_0 = \frac{3.75\psi\vartheta C_v^*}{(C_v^*/R)M}$$

$$B_i = a_i + b_i\omega$$

$$\text{for } i = 1, 2, \dots, 7$$

$$q = \frac{0.003586}{V_c^{2/3}} \sqrt{\frac{T_c}{M}}$$

$$y = \frac{V_c}{6v}$$

$$G_1 = \frac{1 - 0.5y}{(1 - y)^3}$$

$$G_2 = \frac{\frac{B_1}{y} (1 - \exp(-B_4 y)) + B_2 G_1 \exp(B_5 y) + B_3 G_1}{B_1 B_4 + B_2 + B_3}$$

$$\lambda = 1000 \left[\frac{31.2\vartheta\psi}{M} \left(\frac{1}{G_2} + B_6 y \right) + q B_7 y^2 T_r^{0.5} G_2 \right]$$

where

The constants are

$$A = 1.16145, B = 0.14874, C = 0.52487, D = 0.77320, E = 2.16178, F = 2.43787, a_1 = 2.4166, a_2 = -0.50924, a_3 = 6.6107, a_4 = 14.543, a_5 = 0.79274, a_6 = -5.8634, a_7 = 91.089,$$

$b_1 = 0.74824$, $b_2 = -1.5094$, $b_3 = 5.6207$, $b_4 = -8.9139$, $b_5 = 0.82019$, $b_6 = 12.801$, $b_7 = 128.11$

k is in mW/m.K, T is in Kelvin and P is in Pascal (Pa).

In order to calculate thermal conductivity using this method, we need additional information of specific volume at critical point and molecular weight of the fluid. For CO₂, critical molar volume (V_c) is $94.07 \times 10^{-6} \text{ m}^3/\text{mole}$ and molecular weight (M) of CO₂ is 44.01 gr/gr.mole. It also needs the specific volume at corresponding P and T ($v(T, P)$), and the ideal gas constant volume specific heat, $C_v^*(T)$ which is function of temperature only. The latter can be found from the correlation for ideal gas constant pressure specific heat $C_p^*(T)$, subtracted by R , gas constant ($R = 8.3145 \text{ J/mole.K}$).

Because all information to calculate thermal conductivity are known or at least can be estimated from other correlation, we are now able to calculate thermal conductivity as the function of pressure and temperature in our area of interest. The results are plotted, compared and analyzed. The reference for this property is taken from Vesovic et al. [26]. We have also another comparison material which taken from PVTsim software.

Special for the case mentioned below, TOTAL [7] gives the recommendation of correlations used for estimating thermal conductivity as follow:

- Liquid thermal conductivity under 1 bar below normal boiling temperature and at vapor pressure when the liquid is above normal boiling point temperature. It is valid for the range of temperature 216.58 – 300 K

$$\lambda^L = A + BT + CT^2$$

where

$$A = 0.4406, B = -1.2175 \times 10^{-3}, C = 0$$

- Vapor thermal conductivity under 1 bar above normal boiling temperature and at vapor pressure when the vapor is below normal boiling point temperature. It is valid for the range of temperature 194.67 – 1500 K

$$\lambda^v = \frac{AT^B}{1 + \frac{C}{T} + \frac{D}{T^2}}$$

where

A = 3.69, B = -0.3838, C = 964, D = 1.86 x 10⁻⁶.

This recommendation are checked and compared with other sources as well.

2.2.10 CO₂ T-S Diagram

After all properties above have been calculated we can construct T-S diagram for CO₂. The purpose of constructing T-S diagram is to visualize the PVT behavior of fluid in connection with the processes bear by fluid.

T-S diagram is the plot of Temperature versus Entropy. In the diagram, we can make isobars line, isenthalpy's line, isochorics line and etc. The vertical lines itself represent isentropy's while the horizontal lines represent isotherms. All the theoretically possible processes when the fluid is moved from one state to another state are described in one diagram. The effect of the process to the change of the properties can be easily observed and analyzed to understand and explain the physic and behavior of the fluid.

For example: Isenthalpy line shows that at high pressure isenthalpy expansion causes the temperature to decrease while at moderate pressure, isenthalpy expansion causes the decrease of temperature and then become flattened when the pressure becomes very low which means no temperature changes. This is agree well with the theory that says ideal gas has JT coefficient equal to zero and at very low pressure, real gas behaves similar to ideal gas.

Another example is expansion at constant entropy (Adiabatic reversible) which represented by vertical line in T-S diagram, shows that the expansion always causes the decrease of temperature. Again it is agree well with the theory. It is many understanding that we can get from this diagram.

To construct this diagram, we need inverse function which is the function to find either pressure or temperature from the value of property itself and pressure or temperature known (i.e. pressure as the function of enthalpy and temperature). Sometime it is very complicated and tedious even may be impossible to find it analytically due to the complexity of the "original" function. Indeed it can be solved numerically but aware must be taken with this method. The "wrong" initial estimate could lead to ineffectiveness of the program even could lead to the wrong result.

Luckily we have some software which can do the inverse calculation to find properties and/or parameters from the two known variables even though it is “limited” of pressure and temperature range (e.g. ALLPROPS, limited on the range 0 – 1000 bara and 0 – 1000 K). In this work, we used ALLPROPS to construct CO₂ T-S Diagram.

2.3 HYDRAULICS OF CO₂ INJECTION

2.3.1 INJECTION MODEL

One of the backgrounds of this work is to understand and be able to use the right model for injection well design. The properties part gives the basis to understand the processes that happens in the injection flow of the fluid. Our main concern in this work is to estimate pressure and temperature distribution in the injection pipe/tubing as the fluid is injected downward. Injection process in real life involves a lot of parameters, phenomenon, complexity and other aspects that difficult to be described and to be understood. But, we can do the modeling to approach the real one.

Now a day, the commercial softwares providing the calculation for the design of injection well are available abundantly. Easily we can use it but we may don't know surely the physic of the formula they are using in the software. MGR team at TOTAL found that they had an error circa 15% when using one of the commercial software to make the design of CO₂ injection well. This error is out of their tolerance range for injection well design. Many hypothesis are made to explain it but it is unproved yet. Anyway, this work is not to prove the hypothesis are correct or not, but rather to observe the injection process more intensively starting from the simplest one then developed into more complicated one.

We start our injection model from the simplest one which is single phase pure CO₂ flow in the straight vertical tubing without any heat transferred in/out (Adiabatic) the fluid flow. The injection parameters such as injection mass rate, surface injection pressure and temperature are assumed constant. The property of pipe such as the roughness of pipe is assumed has the same value along the pipe and only one constant diameter along the pipe/tubing.

There are two main stages in injection period, namely transient (unsteady state) period and steady state period. Steady state flow is the central issue here but we also consider a

little part of transient flow using a very simple approach to model it. We also study the static condition of the fluid in the tubing. After all, the sensitivity analysis is done to see the effect of injection parameters to pressure and temperature distribution (except for constant internal energy case and unsteady state flow).

In this work, we limit ourselves into these issues:

- Isothermal static pressure calculation
- Steady state flow approach
 - ❖ Isenthalpy process along the pipe
 - ❖ Un-Isenthalpy process along the pipe
 - Internal energy changes is approximated by friction energy
 - Constant Internal energy
- Unsteady state/Transient flow
 - ❖ Isothermal filling process
 - ❖ Simple approach based on linearity

The simple case is proposed to be used in calculation. This is the data for base case:

Flow direction: Downward (Injection)

Geometry of pipe: Straight vertical, 5200 meters, with one Inside Diameter of 3.5 inches

Property of pipe: One pipe ID of 3.5 inches, homogeneous roughness with dimensionless roughness of 0.0005

Injection parameters: Surface pressure of 30 bara, Surface temperature of 50 °C, and CO₂ mass injection rate of 2.15 kg/s

Assumption: Adiabatic (i.e. no heat in from surrounding to injection fluid and neither from injection fluid to surrounding) and No works are put nor withdrawn in/from the system.

2.3.2 Isothermal static pressure distribution in pipe

For incompressible fluid, the hydrostatic pressure can be easily determined due to the density of fluid is constant. Pressure at any depth can be calculated by adding the hydrostatic term with the reference pressure. Hydrostatic term consists of density, gravity acceleration and vertical distance between reference and the point which its pressure to be calculated. Since the fluid is incompressible, the density is constant everywhere along the pipe. The gravity acceleration value actually is the function of vertical depth relative to earth nucleus but since the variation is very small for our injection case (it is proved latter by the comparison of constant gravity and varying gravity as the function of depth) then we can neglect the variation of gravity acceleration value by assuming the constant value of it. In this work we use the following formula to calculate the gravity acceleration as the function of depth from the sea level:

$$g = 9.81 + 3.086 \times 10^{-6} h$$

It is assumed that the gravity acceleration at sea level is 9.81 m/s^2 . h is measured as the positive value with the unit of meter from sea level vertically downward. The purpose of using this is to view more detail the gravity effect to static pressure calculation.

In hydrostatic formula, the depth term h also measured in the same way with the h for gravity acceleration calculation, only we use the surface/well head as the reference.

Injection fluid is usually at the phase of gas, liquid, or supercritical (absolutely not in solid phase). At gas and supercritical phase, the fluid is compressible where the density changes much due to the change of pressure. In addition to this is the density is the function of pressure and temperature (not only temperature). We can do every static pressure calculation if we know of the distribution of temperature along the pipe. We simplify this by setting the temperature constant along the pipe. Then a question arises: How to calculate the static pressure along the pipe filled with this compressible fluid?

One of methods to solve this problem is using *hydrostatic pressure formula in infinitesimal level and updating the pressure* to calculate the pressure for the next infinitesimal section. In other words, we divided the long pipe into many smaller segments of pipe then we calculate the pressure of the end of first segment using hydrostatic formula assuming constant density for this segment which is obtained as the function of pressure and temperature at the top of the segment. This calculation is continued for other segment with updated pressure and density from the calculated pressure from previous section.

Below is the procedure to do the static pressure calculation base on this method:

- i. Divide the pipe into smaller segments. The smaller the more accurate the result is
- ii. Start with the first segment which P and T are known. Find the density
- iii. Estimate the pressure at the end of the pipe segment using Hydrostatic equation
- iv. This calculated pressure is used to find the new density. Both are used for the calculation for the next segment of pipe.
- v. Repeat above calculation until it covers entire length of pipe

From the procedure above, it is obviously that the accuracy of the calculation is depends on how large our pipe segment is. The smallest is the most accurate and theoretically the true result is at the length of segment is equal to zero which means the number of segments are infinite. But surely we can't use the length of zero in our calculation but we can use the length approaching zero.

It is also obvious that the temperature is independent of pressure. The temperature plays the role in determining the density of each segment. Due to independency of temperature, we can set any temperature for any segment and do the pressure calculation. **So actually with this method, we can do the static pressure calculation for any distribution of temperature along the pipe (as long as it is known).** Here, we only consider constant temperature along the pipe (isothermal with the surface injection temperature).

Other benefit from this method is that we can also calculate the mass of fluid in each segment and/or the total mass in entire pipe. The mass in each segment is important input for the calculation of pressure in isothermal filling scenario of transient flow.

Finally, the sensitivity analysis (changing one parameter of injection and keep the rest of input data the same as the base case) is done to observe the effect of injection parameter to pressure distribution along the pipe.

2.3.3 Steady State Isenthalpy process along the pipe

Steady state flow means the flow which all the “flow properties” are independent of time. As the flow taking place, there are neither accumulations nor withdrawals of the fluid in/from the media of flow. The dynamic only happens in space dimension rather than in time. The prerequisite for this kind of flow is the mass in has to be equal to mass out.

To describe the flow of the fluid in the media, at least three equations has to be provided:

- Continuity equation (i.e. mass balance equation)
- Momentum/Impulse equation
- Energy balanced equation (e.g. 1st law of Thermodynamic for open system)

The term steady state implicitly says about the condition of mass balance equation: mass in exactly equal to mass out, no accumulation or withdrawal of the fluid. Momentum equation will lead to the determination of friction force in relation with the flow properties (i.e. the resultant of forces drive the movement of the fluid). The last equation is the general equation but really important one because it explains the process happened in the flow. Almost all the properties and parameters of fluid flow are involved in this equation directly and/or indirectly.

The first law of Thermodynamic for open system can be expressed mathematically as below:

$$\frac{dU_{cv}}{dt} = \dot{Q} - \dot{W} + \dot{m}_i \left(u_i + p_i v_i + \frac{V_i^2}{2} + gz_i \right) - \dot{m}_e \left(u_e + p_e v_e + \frac{V_e^2}{2} + gz_e \right)$$

The subscript *i* and *e* refer to in and exit. U_{cv} (Joule) is the total internal energy of control volume. t (s) is time. \dot{Q} (J/s) is the heat rate exchanged between the system with surroundings (positive for the heat enters the control volume). \dot{W} (J/s) is work exchanged

between the system and surroundings (positive for the work done by system). \dot{m}_i and \dot{m}_e (kg/s) are mass rate in to system and mass rate exit from system respectively. u_i (J/kg) is specific internal energy of the fluid in to system while u_e (J/kg) is specific internal energy of the fluid exit from the system. v_i and v_e (m³/kg) are specific volume of the fluid in to system and exit from system respectively. p_i and p_e (Pa) are the pressure in and exit to/from the system. V_i and V_e (m/s) are the velocity of fluid in and out to/from the system. z_i and z_e (m) is the vertical distance from the inlet and outlet of the system relative to the reference position.

Now if we assume:

- Steady state flow
- Adiabatic (i.e. no heat in or out of the system)
- No work is put or withdrawn in/from the system
- Newtonian fluid

The 1st thermodynamic law equation reduced to

$$u_i + p_i v_i + \frac{V_i^2}{2} + gz_i = u_e + p_e v_e + \frac{V_e^2}{2} + gz_e$$

While definition of specific enthalpy is

$$h = u + pv$$

Then the 1st thermodynamic law can be re-written as:

$$h_i + \frac{V_i^2}{2} + gz_i = h_e + \frac{V_e^2}{2} + gz_e$$

If we assume that the flow holds isenthalpy process along the pipe, then the equation again reduced to:

$$\frac{V_i^2}{2} + gz_i = \frac{V_e^2}{2} + gz_e$$

If we set the inlet as the reference/datum point, then the equation became:

$$\frac{V_i^2}{2} = \frac{V_e^2}{2} - g\Delta h$$

where

Δh is the length of pipe

What we get here is the velocity of the end of pipe if the velocity of the top of pipe is known. As usual the calculation of pressure would be better if we do it in infinitesimal level. It means the length of the pipe has to be as small as possible to get the better accuracy. This calculation ends up with velocity distribution along the pipe. The pressure distribution can be obtained because we can get the density distribution along the pipe due to the merit of this equation:

$$\rho = \frac{\dot{m}}{AV}$$

where A (m²) is the cross section area of the pipe where the flow taking place.

$$A = \frac{1}{4} \pi D^2$$

Pressure is calculated using hydrostatic formula with the density of each segment which obtained from velocity distribution.

Temperature distribution also can be obtained because the pressure distribution now is known. The main keyword here is isenthalpy. Temperature can be calculated as the

function of pressure and enthalpy using the inverse function. Another way is using T-S diagram to estimate the temperature as the function of enthalpy and pressure.

The assumption of isenthalpy process allow the change in internal energy, pressure and density anywhere along the pipe but it restrict that the sum of internal energy and flow work has to be the same to maintain constant enthalpy. Physical meaning of the final energy balance for this particular case indicates that the potential energy changes (due to position of fluid) are changed fully into kinetic energy in the form of velocity. It is analog to free fall of the object from a height without friction. The velocity grows rapidly due to gravity acceleration until reach the highest velocity value at the lowest position the object could be. Anyway, in real life it is impossible to happen where the velocity always grow because the friction also grows and at some point reach equality and stop the velocity growth. Then, it will move with constant velocity.

Another important question in this scenario is “How about the friction?”. The friction forces cause the dissipation of energy from the system forming useless energy (i.e. heat that can’t be used to get the work). Dissipation of energy is related to the entropy of the system. The entropy is one of the contributors in the internal energy changes. As we allow the internal energy to change but not the enthalpy, so the other contributor of internal energy changes has to change as well. It means the friction is being taken care by both of the changes.

We realize that this kind of flow is impossible in real injection case but this scenario is aimed to get the understanding of the kind of processes that occurs at injection fluid flow.

Below is the procedure to calculate the pressure and temperature distribution of isenthalpy scenario:

- i. Divide the pipe into many smaller pipe segments. The smaller the more accurate the result is

- ii. Start from the surface injection pressure and temperature. Calculate the surface injection density and surface injection enthalpy
- iii. Calculate the end velocity of first segment using the final energy balance equation for isenthalpy process along the pipe
- iv. Calculate the end density of first segment using the relation between velocity and density
- v. Estimate the end pressure of first segment using Hydrostatic formula using the surface injection density (It also possible to used the average density)
- vi. Estimate the temperature as the function of calculated pressure and surface injection enthalpy
- vii. Pressure, Temperature, and density calculated are used for the next segment pressure and temperature calculation
- viii. Repeat the calculation for all segments until it cover the entire length of pipe

2.3.4 Steady State Un-Isenthalpy process along the pipe

For un-isenthalpy process in the pipe, we have two sub-scenarios:

- Internal energy changes is approximated by energy dissipated by friction
- Constant internal energy

Both of them are having the same basic assumptions:

- Steady state flow
- Adiabatic (i.e. no heat in or out of the system)
- No work is put or withdrawn in/from the system
- Newtonian fluid

Recall the 1st thermodynamic law for those assumptions above:

$$u_i + p_i v_i + \frac{V_i^2}{2} + gz_i = u_e + p_e v_e + \frac{V_e^2}{2} + gz_e$$

It also can be written as:

$$p_i v_i + \frac{V_i^2}{2} + gz_i = (u_e - u_i) + p_e v_e + \frac{V_e^2}{2} + gz_e$$

The first term at right hand side of the equation is internal energy difference which for reversible exchange between heat and work, can be written as:

$$\Delta u = T\Delta s - p\Delta v$$

It says that internal energy changes are due to two main changes: entropy changes and specific volume/density changes. For the first scenario, we neglect the second term on the right side of equation. We assume that the contribution from specific volume is very

small so it can be neglected. We also assume that the entropy changes are mainly due to energy dissipated by the friction forces against the flow. The energy dissipation by friction is

$$E_{friction} = \frac{1}{2} \left(\frac{\dot{m}}{A\rho} \right)^2 f \frac{\Delta h}{D}$$

f is the friction factor. To get the friction factor we need to calculate Reynolds number, this is where the viscosity enters into the equation. The friction factor can be calculated using many correlations but here we use the correlation from *Colebrook-White*.

$$\text{Re} = \frac{4\dot{m}}{\pi\mu D}$$

$$\frac{1}{\sqrt{f}} = -2 \log \left(\frac{\varepsilon/D}{3.7} + \frac{2.51}{\text{Re}\sqrt{f}} \right)$$

μ (Pa.s) is the viscosity, π is 3.14159265..., ε/D is dimensionless roughness, and Re is Reynolds number. Colebrook-White friction factor is Moody type friction factor.

If we compared the energy balance equation with *Bernoulli's equation* which can be derived purely from momentum equation, we see that the difference is only in internal energy difference term. Bernoulli assumed no friction on the flow (i.e. no dissipation/isentropy). So It suggests that we can approximate this term using the energy dissipated by friction.

Bernoulli's equation from momentum equation:

$$p_i v_i + \frac{V_i^2}{2} + gz_i = p_e v_e + \frac{V_e^2}{2} + gz_e$$

From thermodynamic, as mentioned before, internal energy term is not only contributed by the friction only but because of density changes (compressibility) as well. Then it tells us that Bernoulli's equation also assumed that the fluid is incompressible which is not true for our case where our fluid CO₂ is compressible. A theory says that for the flow with Mach number (the ratio between the velocity of fluid flowing with the speed of the sound in the media of fluid itself) less than 0.3 which is true for our case, then the flow can be considered as incompressible. We believe that this rule of thumb may be not valid for our case because the compressibility effect could be significant. But we still use this approach as approximation to estimate the pressure and temperature distribution along the pipe. The improvement of approach is left for the next work.

The approach for the first scenario is

$$\Delta u = u_2 - u_1 \approx E_{friction}$$

The second scenario is we assume that the internal energy is constant along the pipe. Thus, the internal energy different always equal to zero along the pipe. Energy balance equation is simply turn into Bernoulli's equation. But the assumptions here are no longer isentropy (no friction) and incompressible (constant density) as Bernoulli's flow. Because our fluid is compressible, then the only chance to get into constant internal energy is when

$$T\Delta s = p\Delta v$$

which means that the effect of entropy changes has to be the same with the effect of compressibility. Since the energy is dissipated from the system then the value of Δs is negative leading to the value of Δv also negative. This negative value of specific volume means that the density of the fluid increases implies to the compression process. The equation explicitly says the value of energy dissipated by friction always the same with the value of energy needed to compress the fluid. Note that the energy dissipated by friction is "useless" so it can't be used to produce work.

The approach for the second scenario is

$$\Delta u = u_2 - u_1 = 0$$

Below is the procedure to calculate the pressure and temperature distribution along the pipe with the first approach of un-isenthalpy processes:

- i. Divide the pipe into many smaller pipe segments. The smaller the more accurate the result is
- ii. Start from the surface injection pressure and temperature. Calculate the surface injection density, surface injection viscosity and surface injection enthalpy
- iii. Calculate Reynolds number using the input from ii). Calculate the friction factor and the energy dissipated by friction force.
- iv. Estimate the pressure of the end of pipe segment using Hydrostatic formula with the density from the top of pipe segment
- v. Calculate the density of the end of pipe segment using the energy balance equation
- vi. Calculate the change of enthalpy in the segment which is

$$\Delta h = (u_e - u_i) + p_e v_e - p_i v_i$$
- vii. Calculate the enthalpy of the end of pipe segment which is

$$h_e = h_i + \Delta h$$
- viii. Estimate the temperature of the end of pipe segment as the function of calculated pressure and calculated enthalpy
- ix. Pressure, temperature, and density calculated are used for the next segment pressure and temperature calculation
- x. Repeat the calculation for all segments until it cover the entire length of pipe

Below is the procedure to calculate the pressure and temperature distribution along the pipe with the second approach of un-isenthalpy processes:

- i. Divide the pipe into many smaller pipe segments. The smaller the more accurate the result is
- ii. Start from the surface injection pressure and temperature. Calculate the surface injection density, surface injection viscosity and surface injection enthalpy
- iii. Calculate Reynolds number using the input from ii). Calculate the friction factor and the energy dissipated by friction force.
- iv. Estimate the pressure of the end of pipe segment using Hydrostatic formula with the density from the top of pipe segment
- v. Calculate the density of the end of pipe segment using the energy balance equation
- vi. Calculate the change of enthalpy in the segment which is
$$\Delta h = p_e v_e - p_i v_i$$
- vii. Calculate the enthalpy of the end of pipe segment which is
$$h_e = h_i + \Delta h$$
- viii. Estimate the temperature of the end of pipe segment as the function of calculated pressure and calculated enthalpy
- ix. Pressure, temperature, and density calculated are used for the next segment pressure and temperature calculation
- x. Repeat the calculation for all segments until it cover the entire length of pipe

The results of two approaches are compared to see how large the contribution of internal energy changes in the injection flow in the pipe.

2.3.5 Unsteady State Isothermal filling process

Unsteady state flow means the flow which all “flow properties” are depends on time. The mass in to the system is not longer equal to mass out from the system which implies to accumulation or withdrawal of the fluid. The situation is more complicated if the heats are exchanged between the system and surroundings and/or works are put or withdrawn in/from the system. The energy balance equation is still valid where all the terms are “active” that have to be taken care of.

Unsteady state also means we add another parameter (i.e. time) into the calculation. Thus, all “flow properties” have the relation to the time and can be expressed mathematically. When we want to estimate the flow parameter (e.g. pressure) as the function of time, we also need the other input parameters as the function of time as well. It means many information have to be known in order to estimate the flow parameter. For this work, we are lacking the information such as the how the mass is distributed along the pipe and what is the temperature distribution along the pipe, both as the function of time. But we solved it with a simplified general method to estimate the pressure and temperature distribution along the pipe which one of them named “Isothermal filling”.

Unsteady state is continuing changing parameters with time. It starts with a condition and ends to another condition. In example for pressure distribution calculation, It starts with an initial pressure profile in the pipe (could be static pressure distribution) then move to another pressure profile (could be steady state pressure distribution) as the time elapsed. The pressure profile in between two conditions can be estimated if we know these two conditions (initial and final). It tells us that the boundary conditions are needed in order to calculate the pressure profile’s in between the boundaries condition.

The idea of isothermal filling comes from the early stage of injection. We assume that the injection completion tools are equipped by the bottomhole check valve/one direction valve which prevent the back pressure from reservoir but allow the fluid to flow to

reservoir. This valve will open if the pressure at upstream of pipe reaches a certain value of pressure which is higher than the reservoir pressure. So there is a period from initial condition until the bottomhole check valve is opened due to pressure. This is the period where we compress the fluid in the pipe until its end pressure reach the opening pressure of the valve. We now want to estimate the pressure distribution in the pipe as the function of time and also estimate the time needed from initial condition until the fluid starts to flow into reservoir.

Surely, many assumptions are applied in this approach, such as:

- Adiabatic (i.e. no heat in or out of the system)
- No work is put or withdrawn in/from the system
- Newtonian fluid
- The mass is accumulated/withdrawn homogeneously along the pipe
- Temperature doesn't increased due to compression of fluid

As mentioned before, we need additional information about the temperature as the function of time to calculate the pressure as the function of time. The simplest information is to assume the temperature is constant along the pipe and regardless the time. In this work, we add this assumption into others above.

One method to calculate pressure distribution with assumptions above is to calculate the infinitesimal compressibility factor after the accumulation/withdrawal and match it to compressibility factor as the function of pressure and temperature. In other words, we divide the pipe into some smaller segments, estimate the pressure at the segment, and calculate the compressibility factor after the mass is added / subtracted at each segment then compared it with the compressibility factor as the function of pressure and temperature. If it is match then the estimated pressure is correct one otherwise the new pressure has to be provided until the correct pressure is obtained.

The equations that we need are

$$z = \frac{PV}{nRT}$$

$$z = \frac{v}{v^*}$$

v and v^* are obtained from real gas equation of state and ideal gas law respectively. With this relation we can get z as the function of pressure and temperature $z(P, T)$. n is the mass of fluid in mole unit. V is volume and in our case is equal to volume of pipe segment. The unknown from both equations is only pressure. Using trial and error method, the pressure can be found.

Below is the procedure to calculate the pressure distribution along the pipe using Isothermal filling method:

- i. Divide the pipe into some smaller pipe segments.
- ii. Each segment have the representative initial pressure and mass of the fluid in it and have to be known/mentioned
- iii. Determine an arbitrary small time step (e.g. 10 seconds), the smallest the better.
- iv. Calculate the amount of mass accumulated in the pipe.

$$m_{acc} = \dot{m}t$$

By the assumption of homogeneous distribution of the mass in the pipe, calculate the mass addition in each segment:

$$\Delta m = \frac{m_{acc}}{L} \Delta h$$

where L is the total length of the pipe

- v. Calculate the total mass in each segment

$$m_t = m_{si} + \Delta m$$

where m_{si} is the initial mass in each segment. Note that the initial mass is larger on the very end of the pipe than in the top of the pipe if we use static condition as our initial boundary

- vi. Calculate the mole number from the total mass
- vii. Give the first estimate of pressure of the segment (we can use the initial representative pressure)
- viii. Calculate the compressibility factor from

$$z = \frac{PV}{nRT}$$

- ix. Get the compressibility factor as the function of pressure and temperature from a real gas equation of state
- x. Compared viii and ix, if the same value then the correct pressure has been obtained otherwise re-do the calculation from point vii with the new pressure estimate
- xi. Do the same calculation for the next segments until it covers the entire length of the pipe
- xii. The pressure distribution obtained here is used for the calculation for the next time step (i.e. the initial boundary condition for the new calculation)
- xiii. Stop the calculation when the end pressure of the pipe reach the opening pressure
- xiv. Total time needed to reach point xiii is the estimation of time needed from the fill the injection fluid until it flowing.

Our unsteady state calculation example for this approach, using static pressure distribution with constant temperature of 50 °C as the initial boundary condition, Isothermal of the same temperature in any time step, and valve opening pressure is ca. 27.2 bara as the final boundary condition.

2.3.6 Unsteady state based on linearity

In steady state analysis, the pressure profile along the pipe is not linear but the temperature and internal energy profile are linear. It gives the inspiration to use the linearity as the tool to calculate the pressure distribution from the linearity of temperature and internal energy. In real life, temperature profile is not linear and getting to linear when it approaches steady state condition. Internal energy profile is alleged having the same pattern with temperature profile. But due to the lack of information of properties of the flowing fluid as the function of time, the method gives the initial estimate that may be can be used in advanced development to calculate the transient pressure profile.

The assumptions used in this method:

- Adiabatic (i.e. no heat in or out of the system)
- No work is put or withdrawn in/from the system
- Newtonian fluid
- Temperature profile for each of time is linear
- Internal energy profile for each of time is linear

We introduce the term called “dimensionless time” which is defined as

$$t_D = \frac{t}{t_{ss}}$$

where $0 \leq t \leq t_{ss}$ and t_{ss} is the time to reach the steady state condition.

As before, boundary conditions have to be known in order to calculate the profiles in between. For any given dimensionless time, temperature profile and internal energy profile can be obtained. Then if we have the inverse function which calculates the pressure as the function of temperature and internal energy, the pressure profile is obtained. In other words, for any given time in between initial and steady state time and any position, find the temperature and internal energy on that position based on linearity assumption then find the pressure for that position.

Actually, linearity can be used also even though the boundaries (i.e. the initial and final condition) are not showing linear trend. The linearity here is not the profiles linearity but the linear in the “growth” of the properties with respect to time. Again, it may be not true but it gives the initial approximation and may be used for other methods.

An interesting question arises from this method, “Is the result from this method is the same with when we assumed steady state flow by changing the injection parameter into “equivalent injection parameter”? This question can be answered by comparing the result from this method with the result from steady state flow with adjusted parameter. We did it and the result will be at on result and discussion part.

Together with isothermal filling, this method can perform the sequence of pressure and temperature profiles along the pipe at the early stage of fluid injection and may be also the total time until the flow reach steady state condition. Our example calculation for this method used the static pressure profile as the initial condition and steady state profile as the final condition.

Below is the procedure to estimate the pressure profile using this method:

- Divide the pipe into many smaller segments. The smaller the better
- The initial condition and final condition has to be known. Put the representative initial and final value of pressure and temperature in each segment. Calculate the initial and final value of internal energy of each segment.
- At any given dimensionless time, calculate the temperature and internal energy of the first segment based on the linearity of the values between boundaries.
- Find the pressure as the function of temperature and internal energy
- Re-do the calculation above for all the segments until it covers the entire length of pipe
- Do all the procedure above for others given dimensionless time

3. RESULTS AND DISCUSSION

3.1 CO₂ PROPERTIES CALCULATION EXAMPLE

Problem:

Estimate the density, compressibility factor, enthalpy, entropy, internal energy, constant pressure specific heat, constant volume specific heat and Joule-Thomson coefficient using Peng-Robinson Equation of State. Estimate also viscosity and thermal conductivity CO₂ at P = 30 bar absolute and T = 50 °C. The reference for enthalpy, entropy and internal energy is P = 1 bar absolute and T = 300 K.

Solution:

Input data needed in PR-EOS are

$$P = 30 \text{ bara} = 3 \times 10^6 \text{ Pascal}$$

$$T = 50 \text{ °C} = 323.15 \text{ K}$$

$$R = 8.3145 \text{ J/mol.K, for CO}_2, R_o = 188.923 \text{ J/kg.K}$$

$$T_c = 304.12 \text{ K}$$

$$P_c = 7.374 \times 10^6 \text{ Pascal}$$

$$V_c = 0.0021374 \text{ m}^3/\text{kg}$$

$$M = 44.01 \text{ gr/gr.mole}$$

$$\omega = 0.225$$

From PR-EOS, we get:

$$T_r = 1.0626, P_r = 0.4068, f\omega = 0.708, a_c = 0.3965 \text{ Jm}^3/\text{mole}^2, \alpha = 0.9568, a(T) = 0.3794 \text{ Jm}^3/\text{mole}^2, b = 2.6678 \times 10^{-5} \text{ m}^3/\text{mole}, v = 0.0176 \text{ m}^3/\text{kg}$$

Density:

$$\rho = 1.2909 \text{ mole/dm}^3 = 56.8113 \text{ kg/m}^3.$$

From ideal gas law:

$$v^* = 0.02035 \text{ m}^3/\text{kg}$$

Compressibility factor z:

$$z = 0.865$$

For enthalpy, entropy and Internal Energy, the reference point is 300 K and 1 bara.

$$(h_2 - h_1) = (h_1^* - h_1) - (h_2^* - h_2) + (h_2^* - h_1^*)$$

$$(h_1^* - h_1) = 41 \text{ J/mole} = 931.61 \text{ J/kg}$$

$$(h_2^* - h_2) = 1189.9 \text{ J/mole} = 27037.04 \text{ J/kg}$$

$$(h_2^* - h_1^*) = 874.2 \text{ J/mole} = 19863.67 \text{ J/kg}$$

The enthalpy:

$$h = -274.7 \text{ J/mole} = -6241.76 \text{ J/kg}$$

$$(s_2 - s_1) = (s_1^* - s_1) - (s_2^* - s_2) + (s_2^* - s_1^*)$$

$$(s_1^* - s_1) = 0.1 \text{ J/mole.K} = 2.27 \text{ J/kg.K}$$

$$(s_2^* - s_2) = 2.6 \text{ J/mole.K} = 59.08 \text{ J/kg.K}$$

$$(s_2^* - s_1^*) = -25.47 \text{ J/mole.K} = -578.79 \text{ J/kg.K}$$

The entropy:

$$s = -27.97 \text{ J/mole.K} = -635.6 \text{ J/kg.K}$$

$$(u_2 - u_1) = (u_1^* - u_1) - (u_2^* - u_2) + (u_2^* - u_1^*)$$

$$(u_1^* - u_1) = 27.4 \text{ J/mole} = 622.59 \text{ J/kg}$$

$$(u_2^* - u_2) = 827.1 \text{ J/mole} = 18793.46 \text{ J/kg}$$

$$(u_2^* - u_1^*) = 681.7 \text{ J/mole} = 15489.66 \text{ J/kg}$$

The Internal Energy:

$$u = -118 \text{ J/mole} = -2681.21 \text{ J/kg}$$

From PR-EOS we also get:

$$T \int_v^{\infty} \left[\left(\frac{\partial^2 P}{\partial T^2} \right)_v \right] dv = -0.954 \text{ J/mole.K} = -21.68 \text{ J/kg.K}$$

$$T \frac{\left(\frac{\partial P}{\partial T} \right)_v^2}{\left(\frac{\partial P}{\partial v} \right)_T} = -15.161 \text{ J/mole.K} = -344.49 \text{ J/kg.K}$$

Poling et al. correlation to find the ideal gas specific heat, we get:

$$C_p^* = 38.26 \text{ J/mole.K} = 869.35 \text{ J/kg.K}$$

Constant pressure specific heat:

$$C_p = 46.061 \text{ J/mole.K} = 1046.6 \text{ J/kg.K}$$

Constant volume specific heat:

$$C_v = 30.9 \text{ J/mole.K} = 702.11 \text{ J/kg.K}$$

$$\left(\frac{\partial v}{\partial T} \right)_p = 3.7583 \times 10^{-6} \text{ m}^3/\text{K}$$

Joule-Thomson coefficient:

$$JT = 0.9549 \text{ K/bar}$$

Viscosity can be estimated using Chung et al and Reichenberg method we get:

$$\eta_0 = 15.918 \text{ mW/mK}, r = 1.0739$$

Viscosity:

$$\eta = 17.095 \text{ mW/m.K}$$

Using Chung et al. method to estimate thermal conductivity, we get:

Thermal conductivity:

$$k = 20.174 \text{ mW/m.K}$$

3.2 CO₂ Properties Results and Discussion

3.2.1.1 CO₂ Phase diagram (P - T plot)

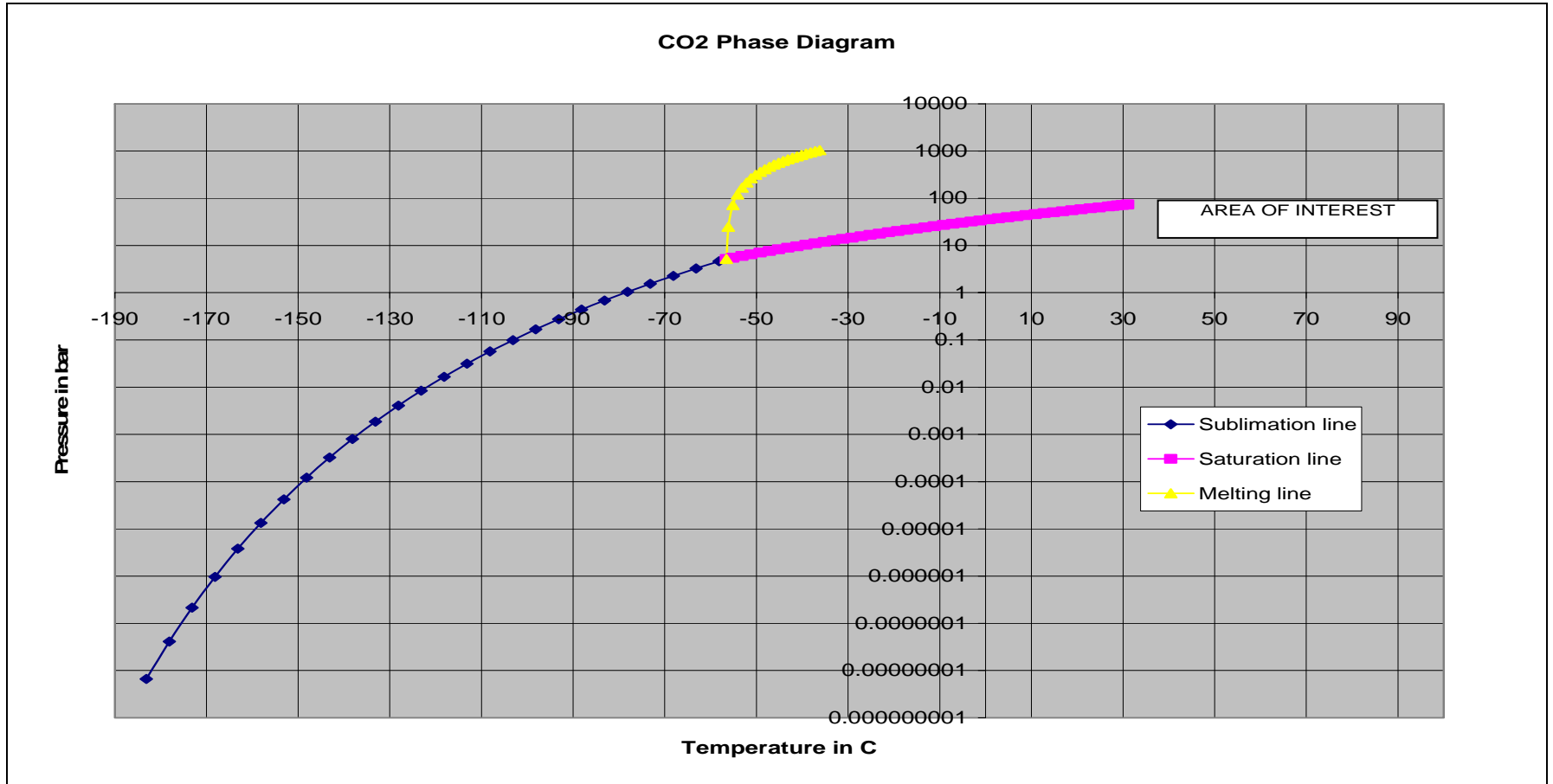


Fig. 3.2.1.1 CO₂ P-T Plot (taken from Angus et al. [1])

3.2.1.2 Comparison of CO₂ vapor pressure

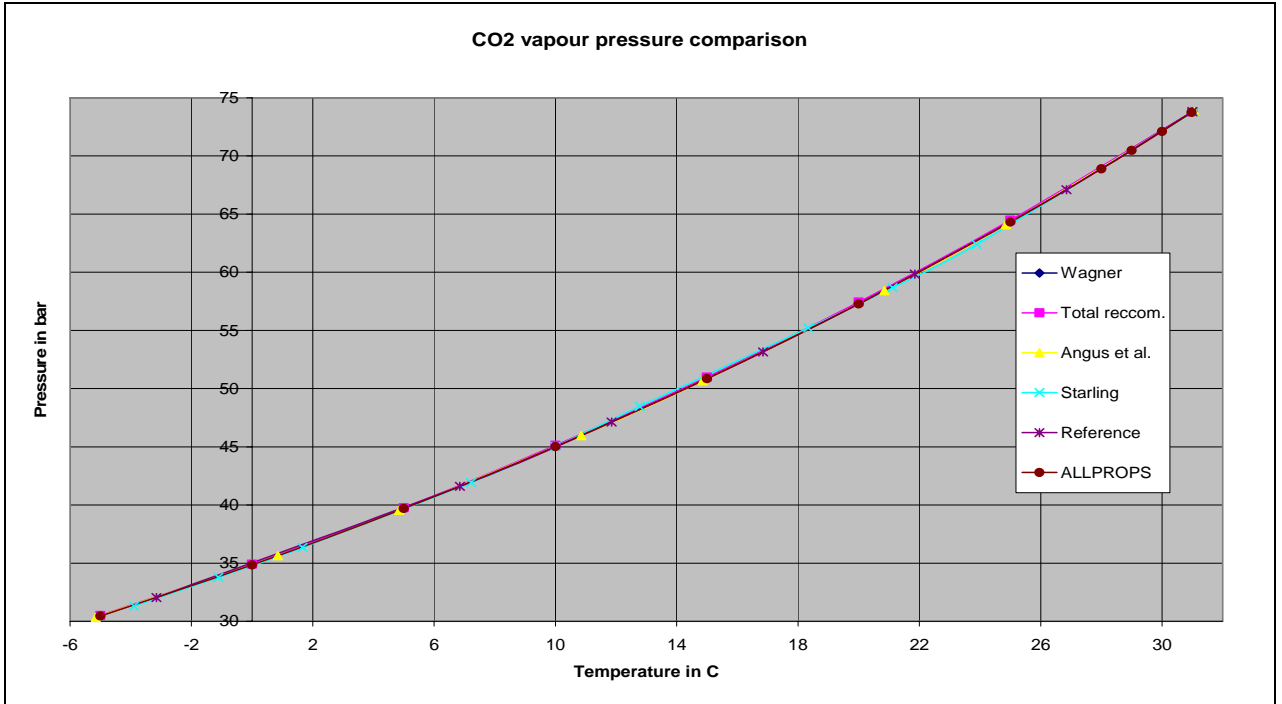


Fig. 3.2.1.2 CO₂ vapor pressure comparison

Figure above shows the agreement of every method in predicting the vapor pressure of CO₂ as the function of temperature. The value different is in the level of the second or third decimal behind the comma if the pressure unit is bara. This agreement says that we can use any of above methods to estimate the vapor pressure of CO₂ as the function of temperature.

3.2.2.1 CO₂ Density-Pressure plot

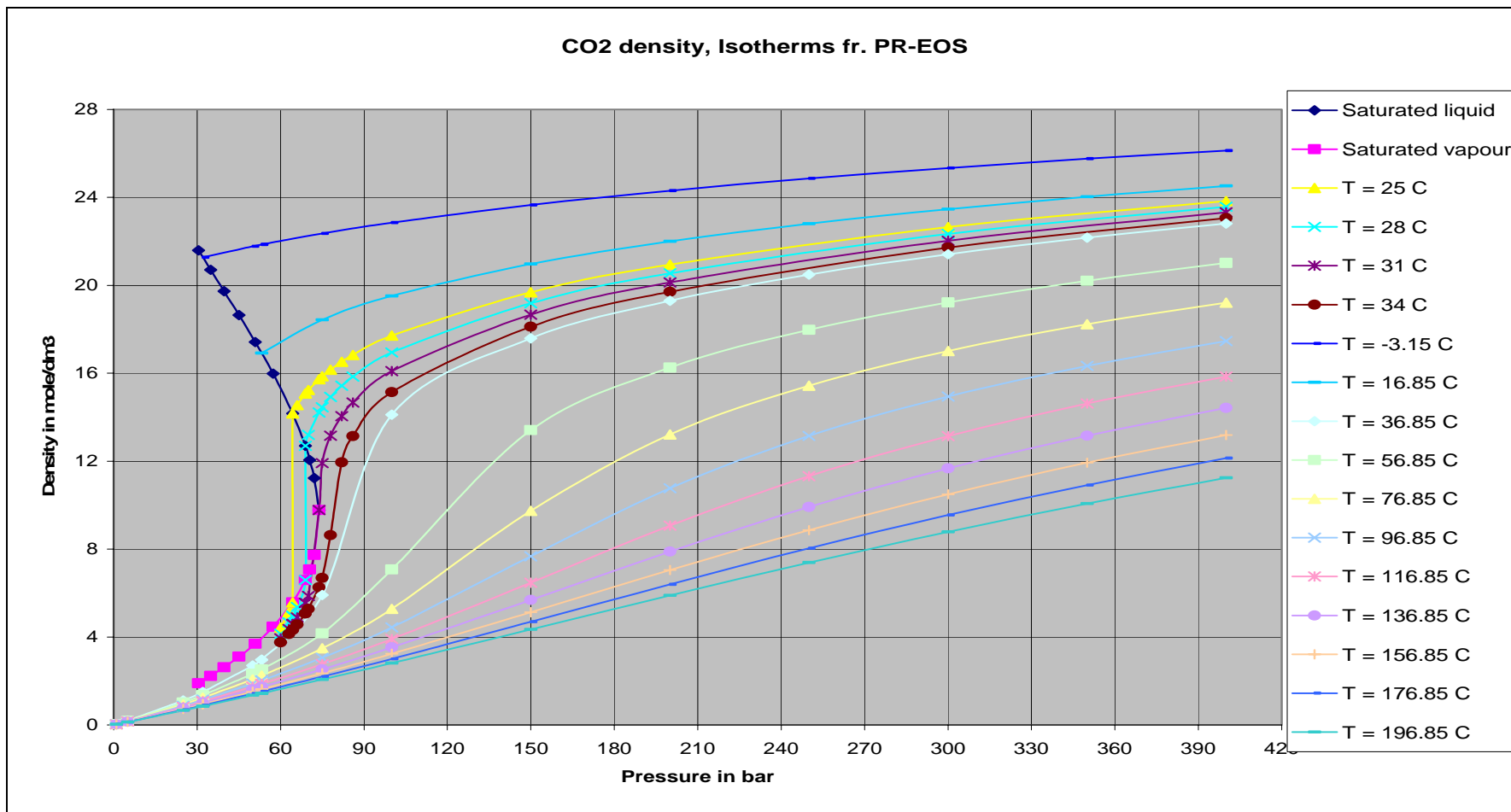


Fig. 3.2.2.1 CO₂ Density-Pressure plot for many isotherms (obtained from PR-EOS)

3.2.2.2 Comparison of CO₂ Density

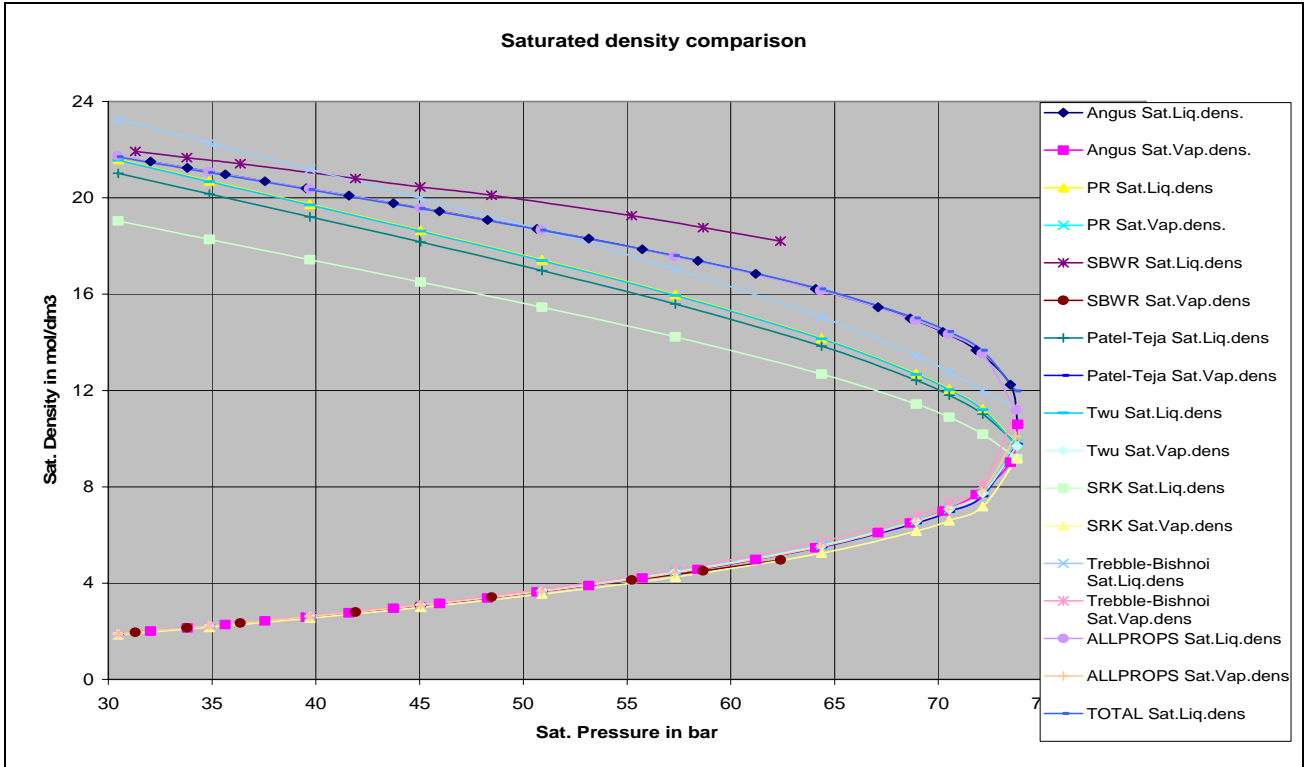


Fig. 3.2.2.2 Saturated CO₂ density comparison

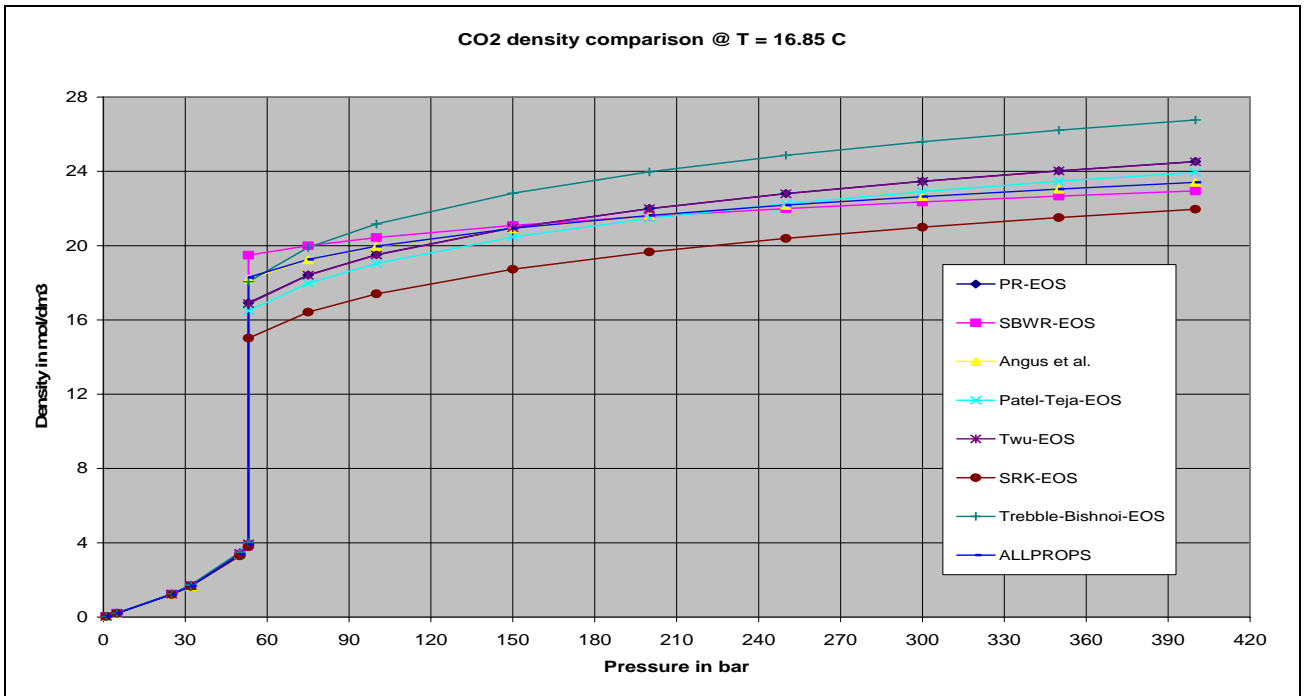


Fig. 3.2.2.3 CO₂ density comparison at T = 16.85 °C

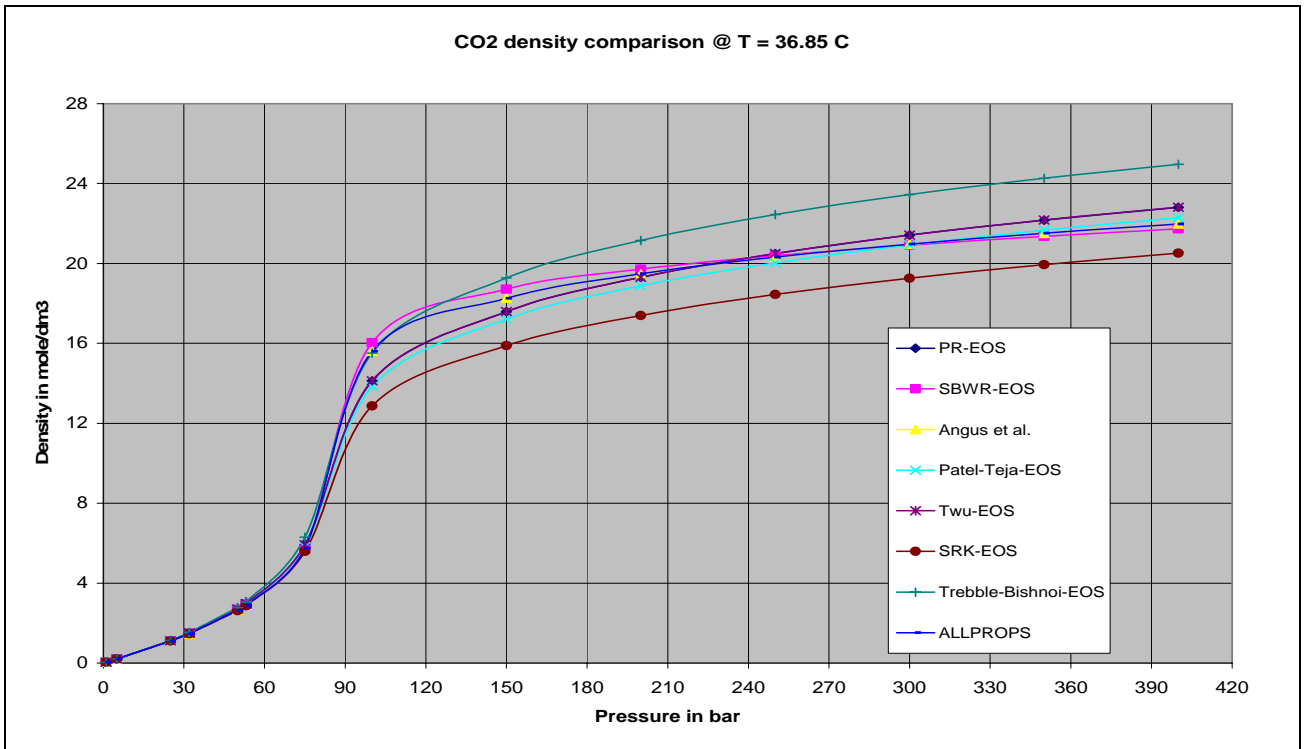


Fig. 3.2.2.4 CO₂ density comparison at T = 36.85 °C

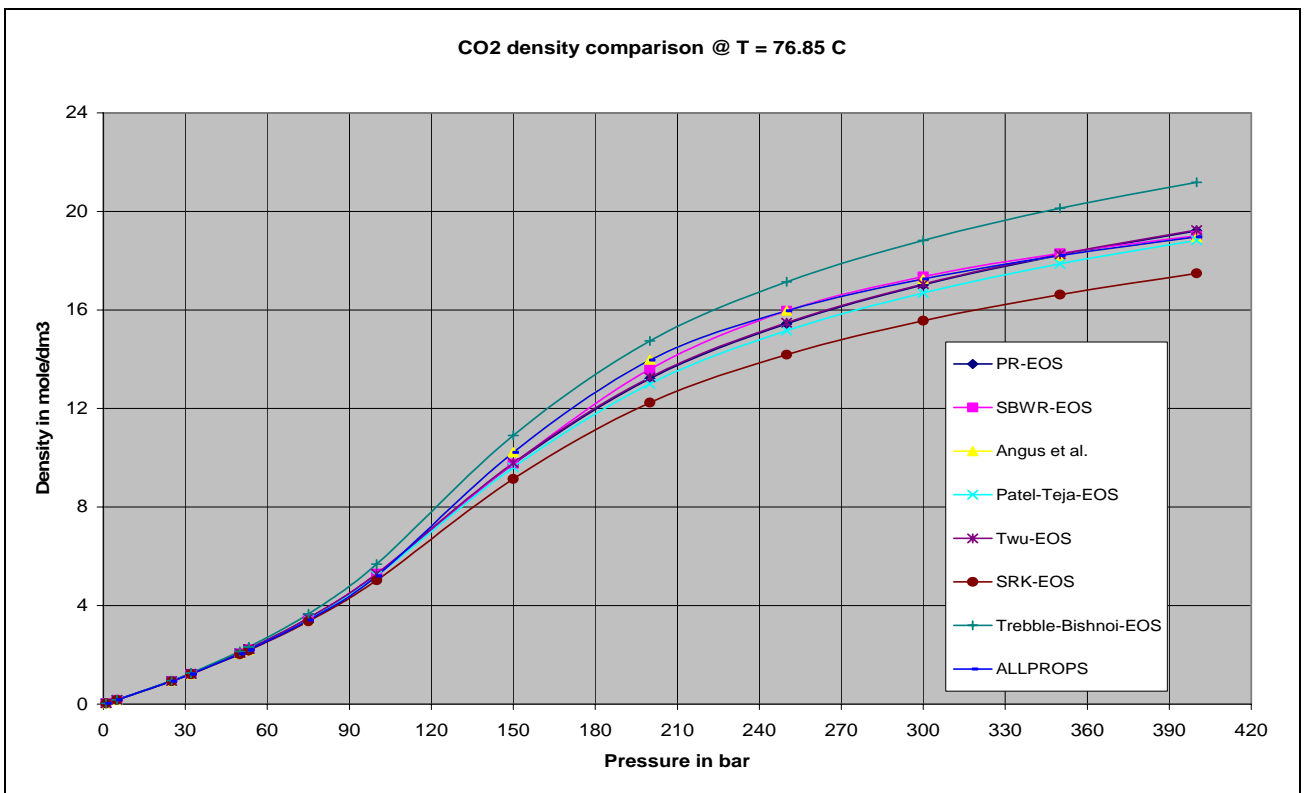
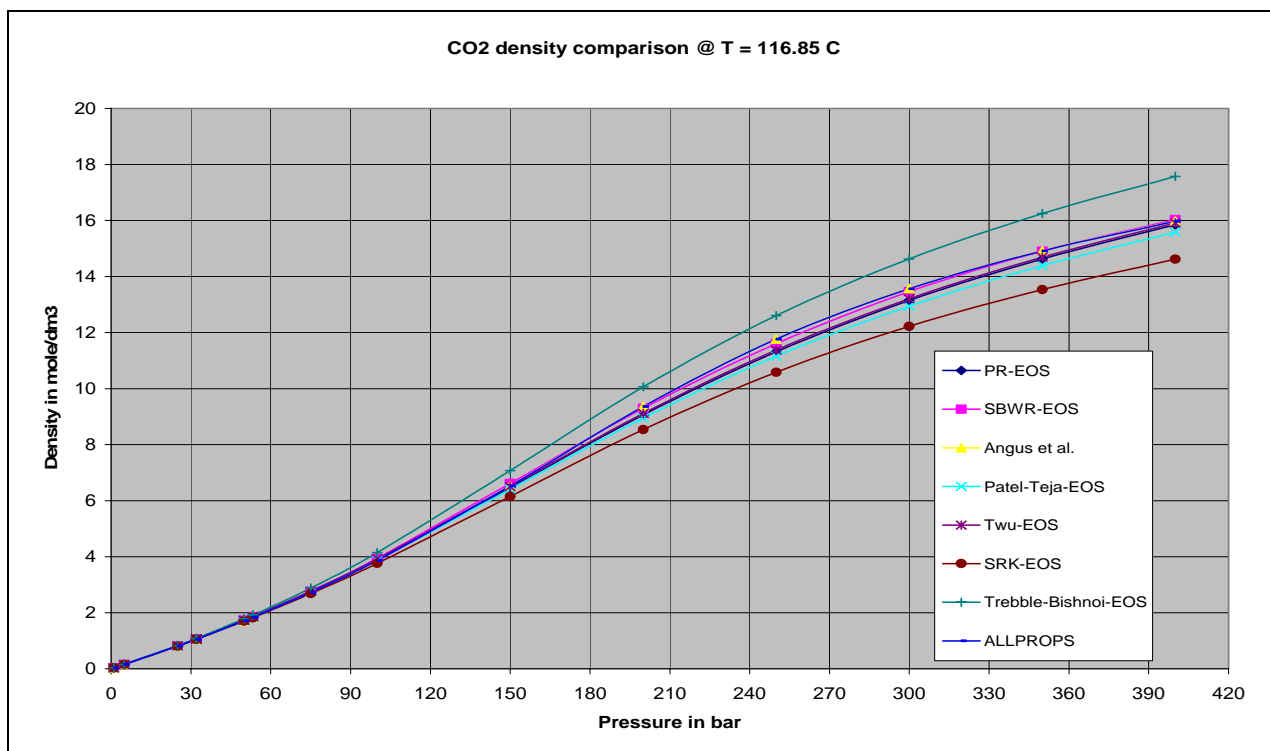
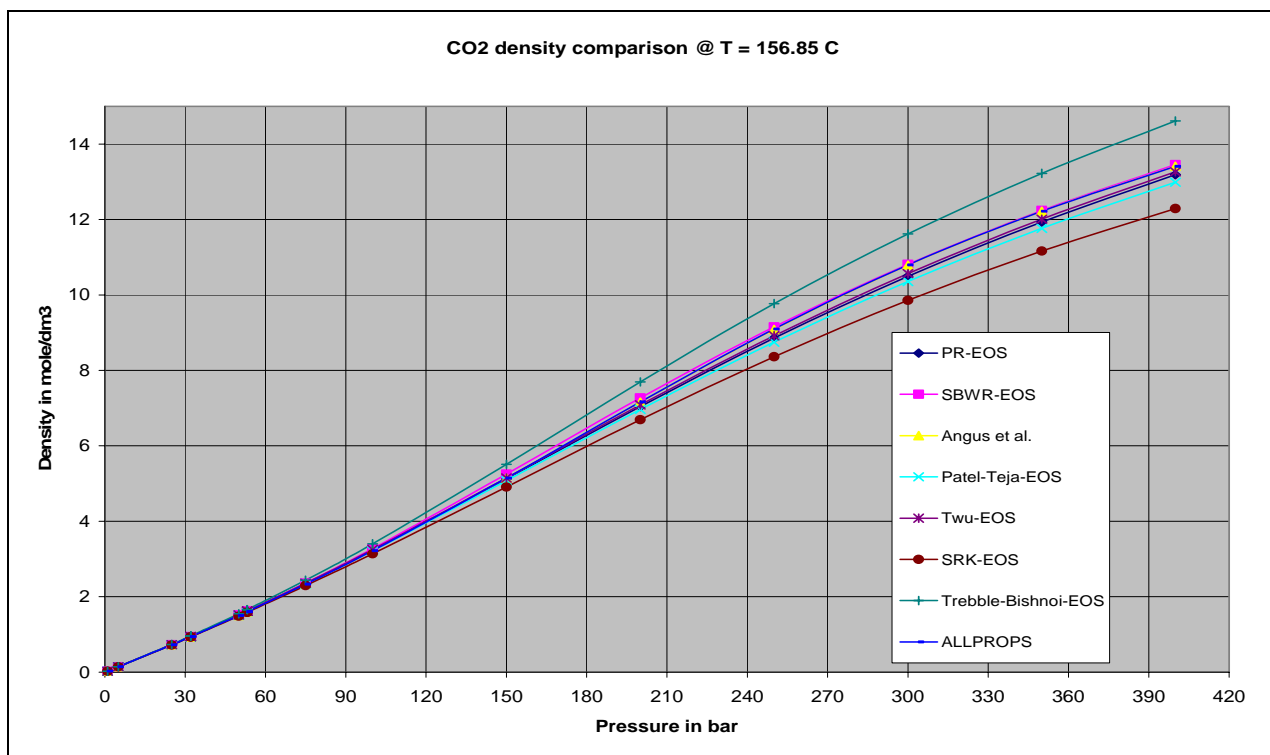


Fig 3.2.2.5 CO₂ density comparison at T = 76.85 °C

Fig. 3.2.2.6 CO₂ density comparison at T = 116.85 °CFig. 3.2.2.7 CO₂ density comparison at T = 156.85 °C

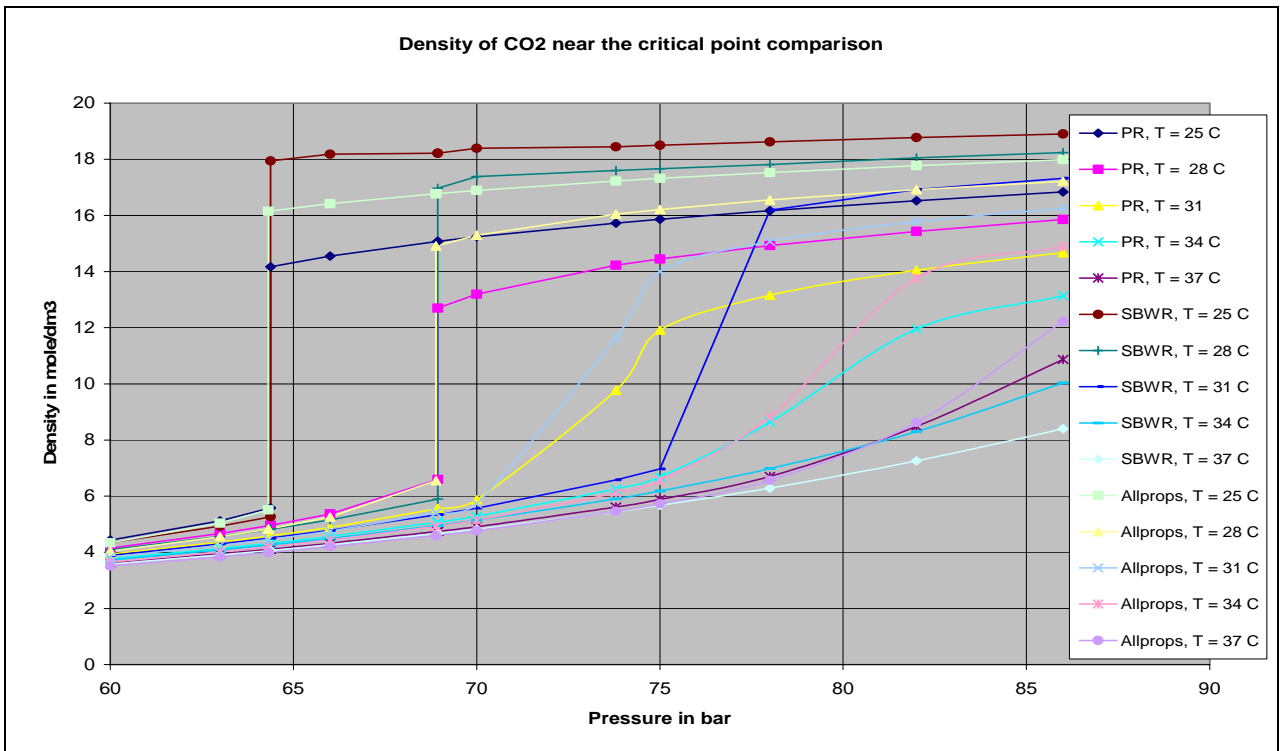


Fig 3.2.2.8 CO₂ density comparison near critical area comparison

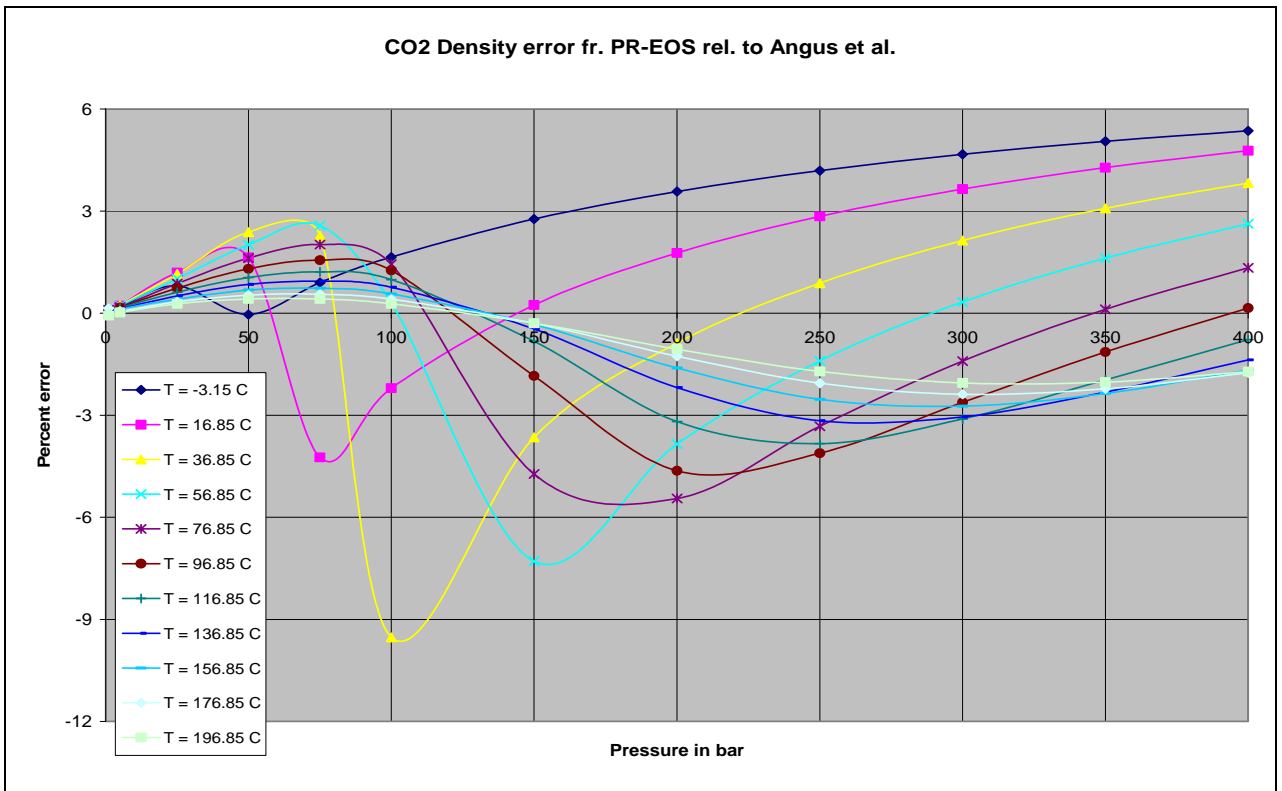


Fig. 3.2.2.9 CO₂ density percent error from Peng-Robinson EOS

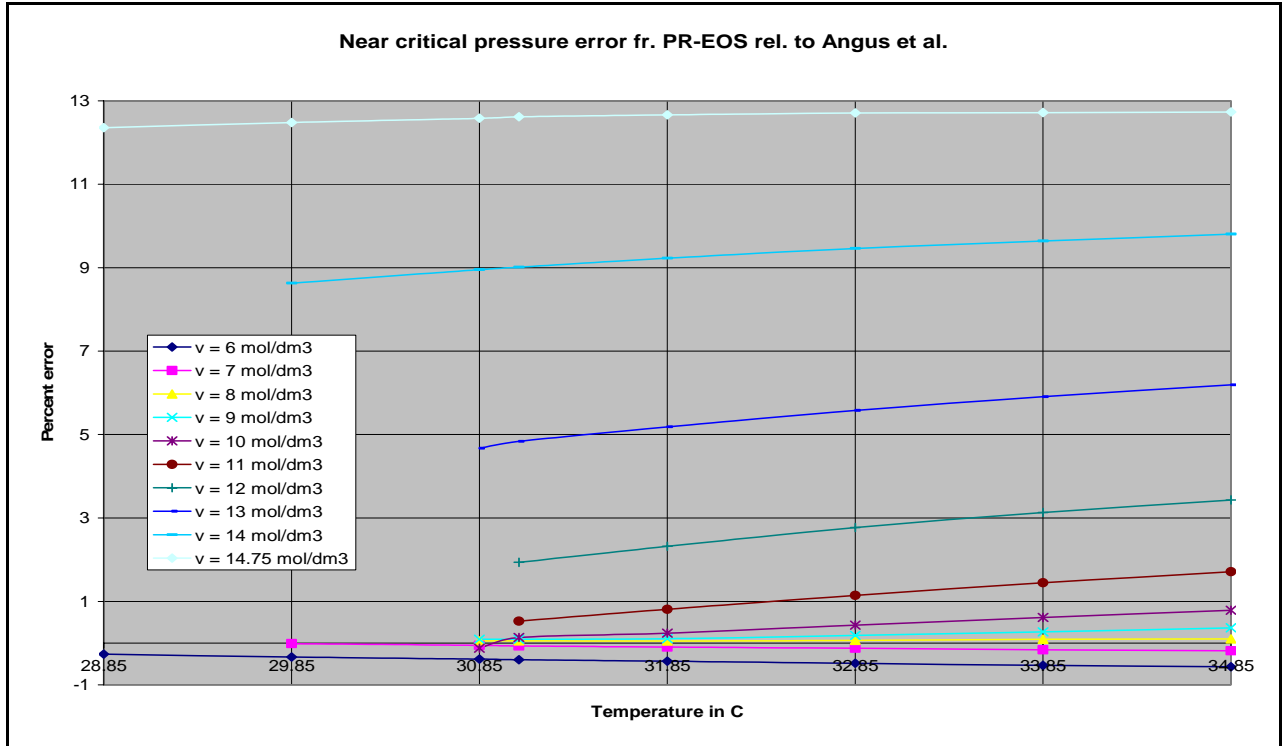


Fig. 3.2.2.10 CO₂ pressure percent error near critical area from Peng-Robinson EOS

Some important points that we get from figures above:

- Pressure has the opposite effect with temperature to density. The increase of pressure at constant temperature always causes the increase of density while the temperature increases at constant pressure always causes the decrease of density.
- “Which more dominant, the effect of pressure or temperature when the fluid moves from one state to another?” The answer is it depends on the “zone” where initial state is located. At area near critical point the density changes much with the changes of pressure and/or temperature (e.g. both may be equal). In some area (e.g. high pressure and low temperature), pressure influence more than temperature which means the temperature changes give insignificant density changes if compared with pressure influences. In other area, temperature is more influencing than pressure.
- Every equation of state (EOS) used in this work is able to predict CO₂ gas phase density accurate enough but not in liquid phase. This fact is seen in every plot.

- Deviation of density value between each EOS is getting larger with the increase of pressure and getting better with the increase of temperature. It means that the higher uncertainty in density prediction by equation of state's is at high pressure and low temperature (i.e. toward to compressed liquid area)
- Each EOS interprets in different way of how the density changes due to the change of pressure and/or temperature at critical area zone. This responsible for the large error at error analysis
- Below is the table of percent error relative to the reference of CO₂ density predicted by some EOS's. The values are the extreme value that the error could reach in the particular area. It is not the average error in that area. The purpose of this is to give the vision on how much the error could be.

Method	Density percent error		Density percent error	
	Area of interest		0<T>200 C & 1<P<400 bara	
	Min.	Max.	Min.	Max.
Peng-Robinson	0.5	3	-10	6
Twu	0.5	3	-10	6
Starling-BWR	0	2	-5	4
Patel-Teja	0.4	2	-12	3
Soave-Redlich-Kwong	-3	0	-18	0
Trebble-Bishnoi	2	10	-1	15
ALLPROPS	-0.2	-0.1	-0.4	0.3

Table 3.2.2.1 CO₂ density percent error at area of interest

- The table below shows the pressure percent error in near critical area :

Method	Pressure percent error	
	Area of interest	
	Min.	Max.
Peng-Robinson	-1	13
Twu	-1	13
Starling-BWR	0	12
Patel-Teja	-1	17
Soave-Redlich-Kwong	0	35
Trebble-Bishnoi	-3	5
ALLPROPS	-0.2	0.2

Table 3.2.2.2 CO₂ pressure percent error near critical area

- The error values above are obtained using the reference: Angus et al. [1]. It was published at 1971 as a monograph and was IUPAC standard. From all methods used to estimate CO₂ density, ALLPROPS is the closest one to the reference while the cubic equation of state's are in the range less than 20 % error when predicting density and/or pressure. Again, this is not the average error value but the extreme value where the error could be.

3.2.3.1 CO₂ Viscosity-Temperature plot

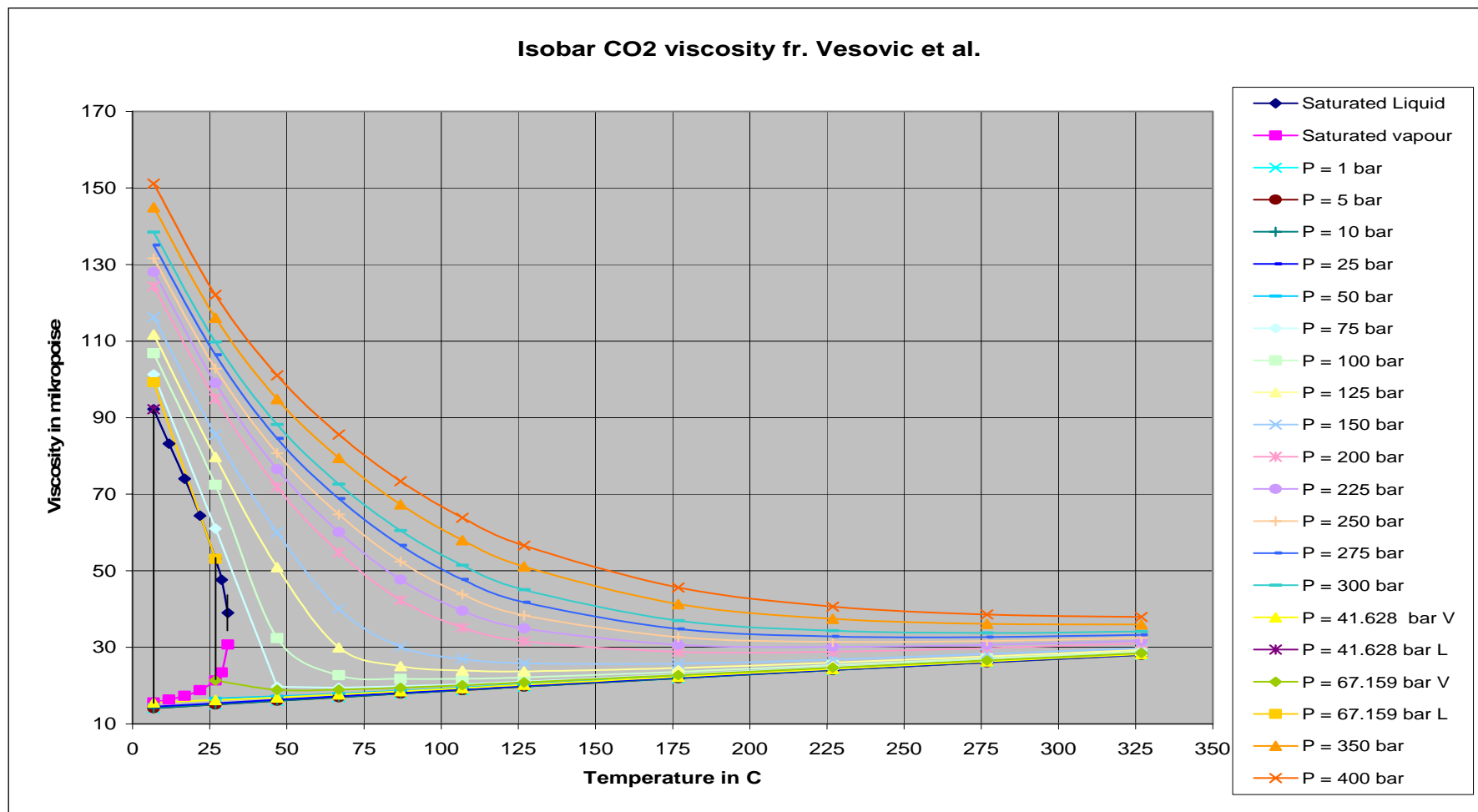


Fig. 3.2.3.1 CO₂ Viscosity-Temperature plot for many isobars (taken from Vesovic et al.)

3.2.3.2 Comparison of CO₂ Viscosity

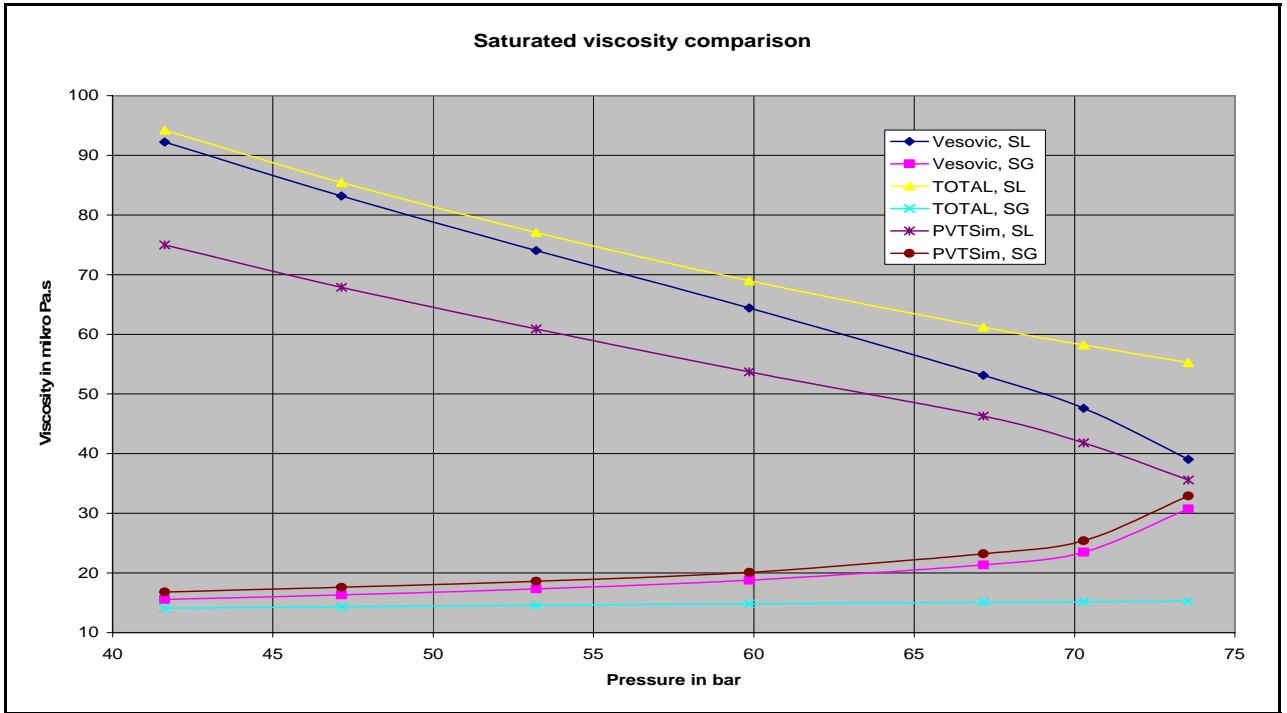


Fig. 3.2.3.2 Saturated CO₂ viscosity comparison

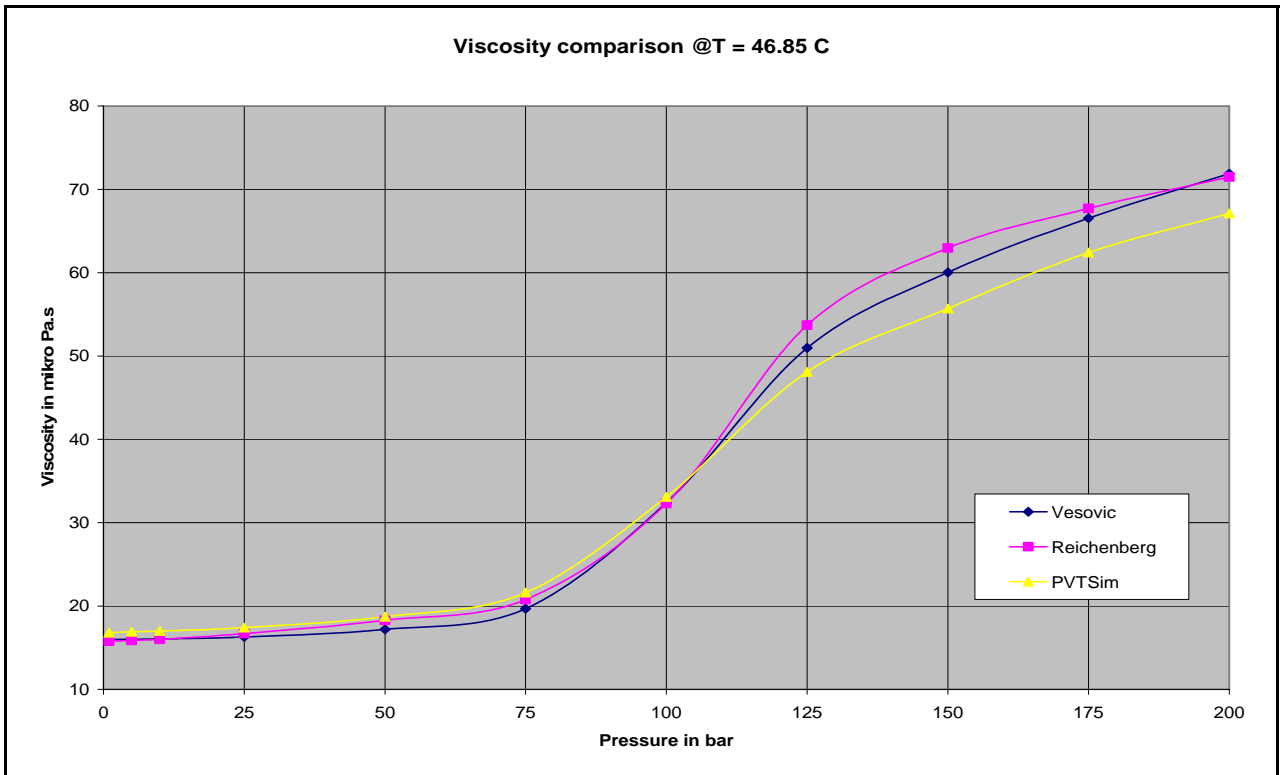


Fig. 3.2.3.3 CO₂ viscosity comparison at T = 46.85 °C

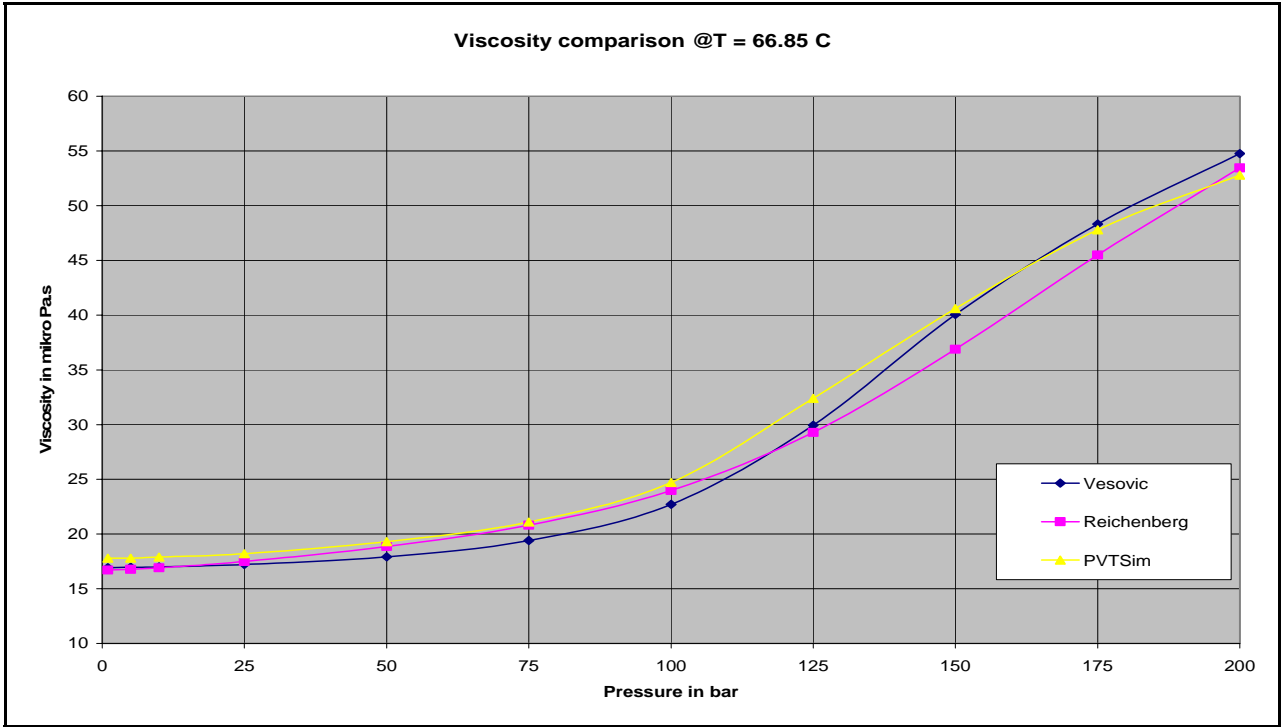


Fig. 3.2.3.4 CO₂ viscosity comparison at T = 66.85 °C

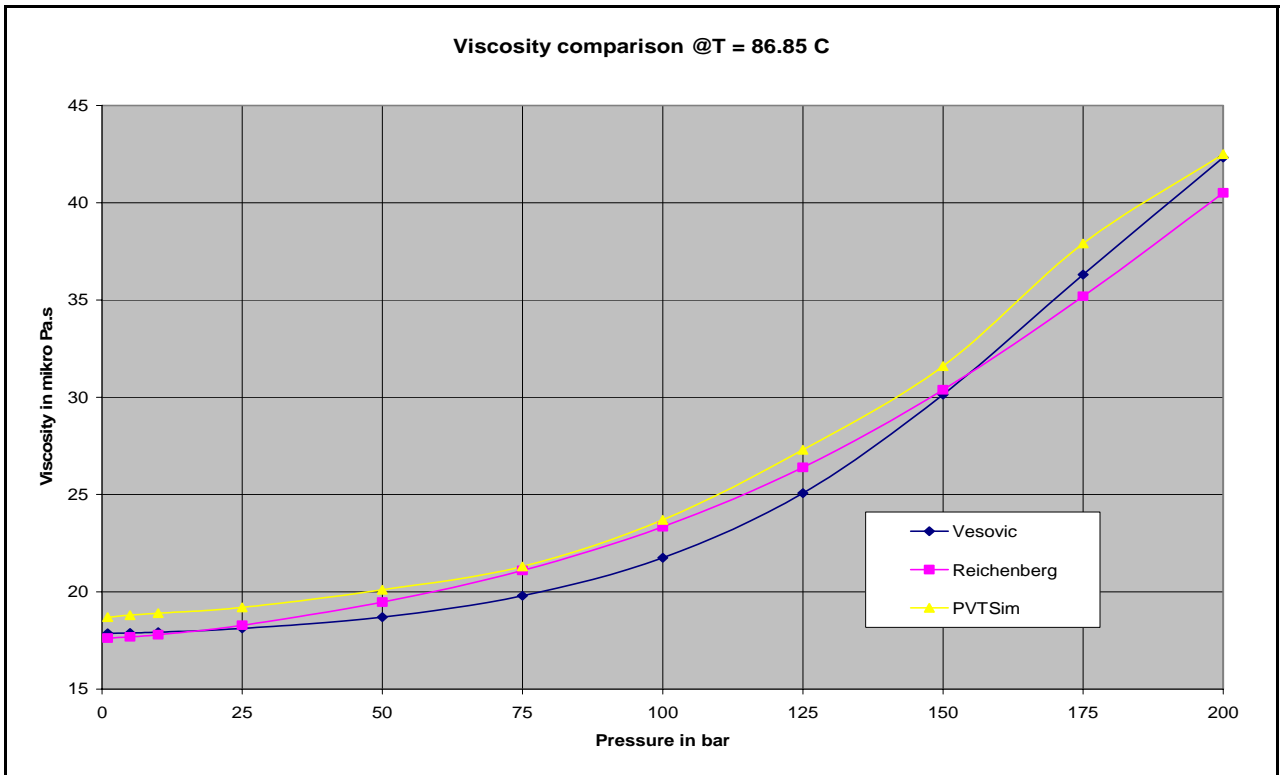


Fig. 3.2.3.5 CO₂ viscosity comparison at T = 86.85 °C

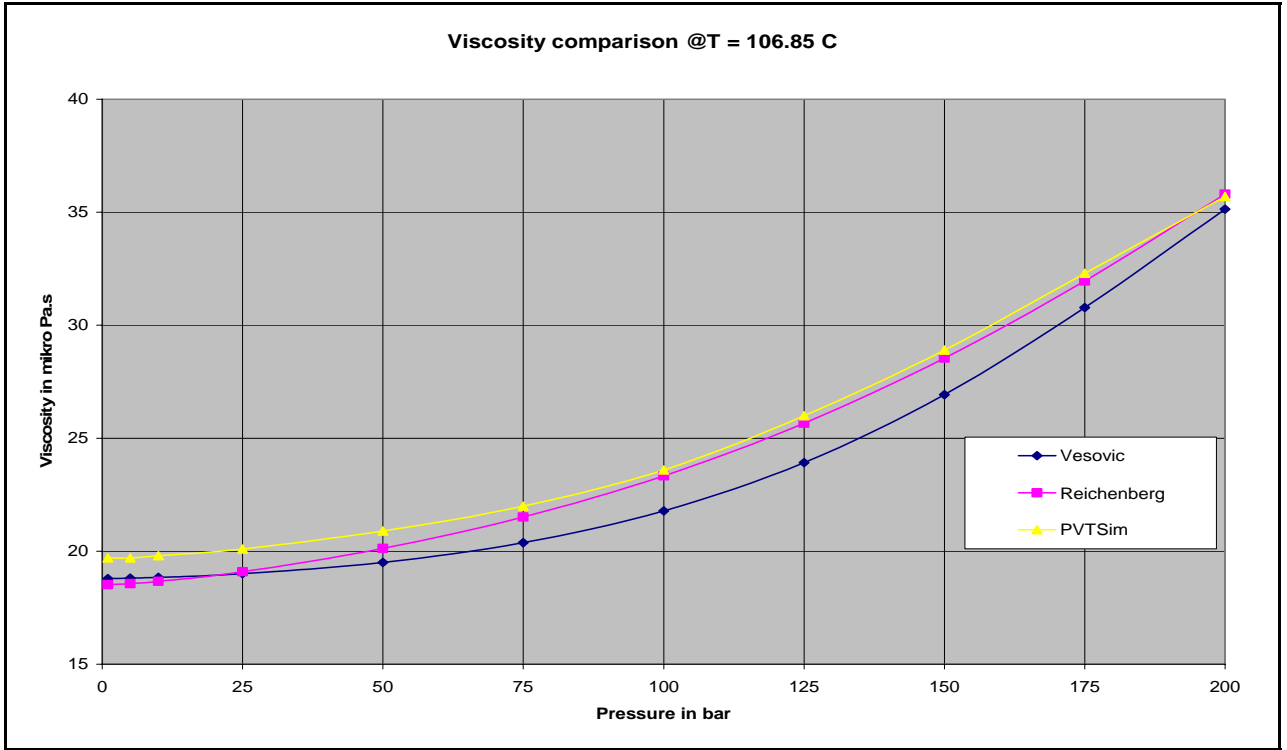


Fig. 3.2.3.6 CO₂ viscosity comparison at T = 106.85 °C

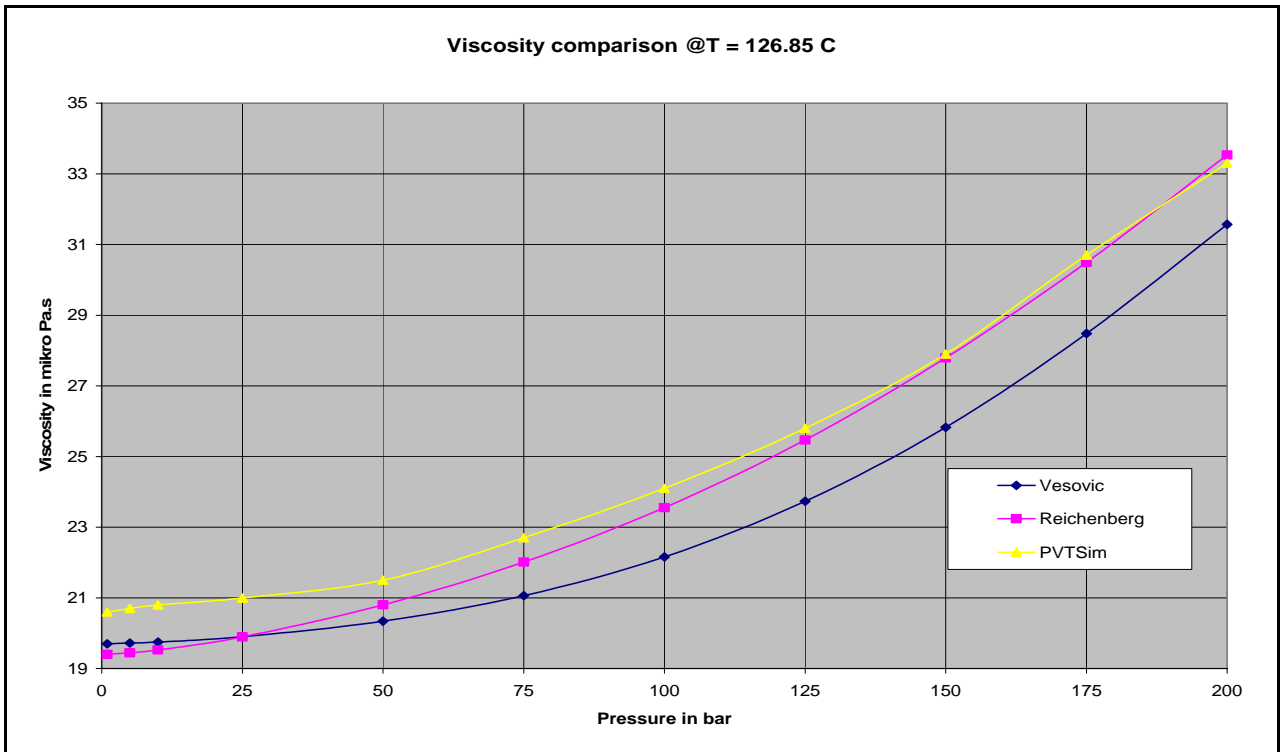


Fig. 3.2.3.7 CO₂ viscosity comparison at T = 126.85 °C

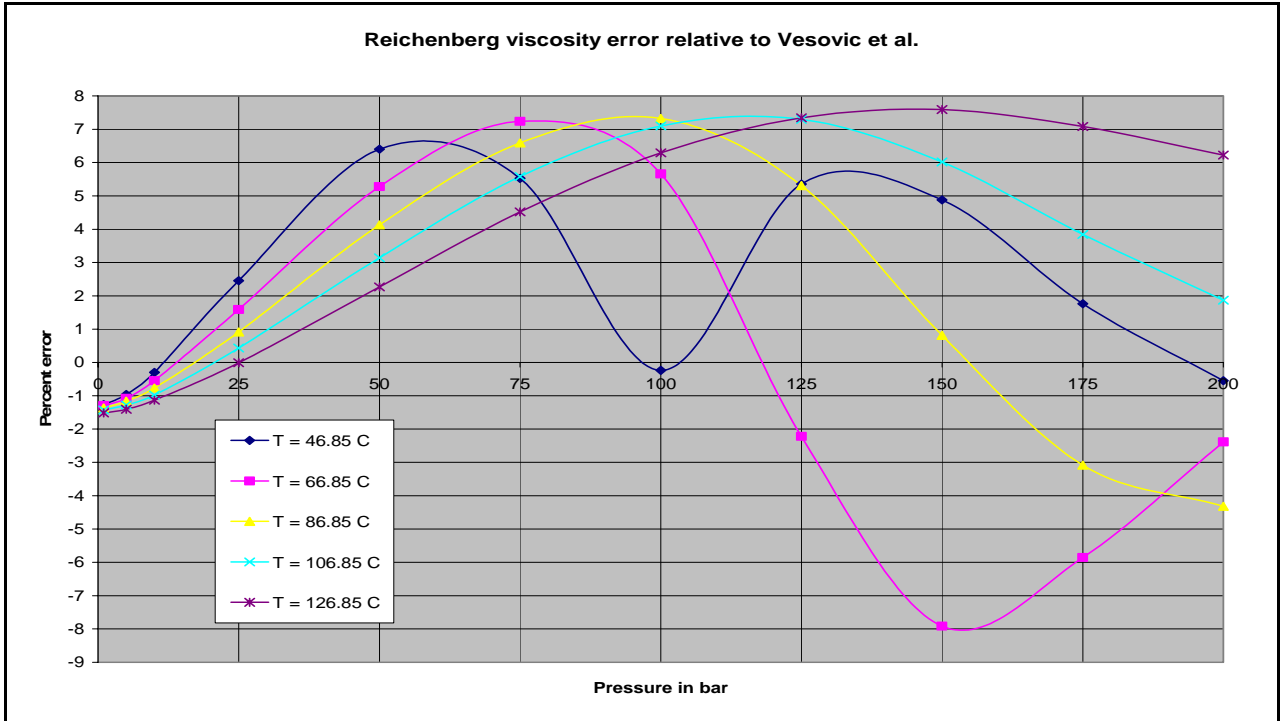


Fig. 3.2.3.8 CO₂ viscosity percent error at area of interest

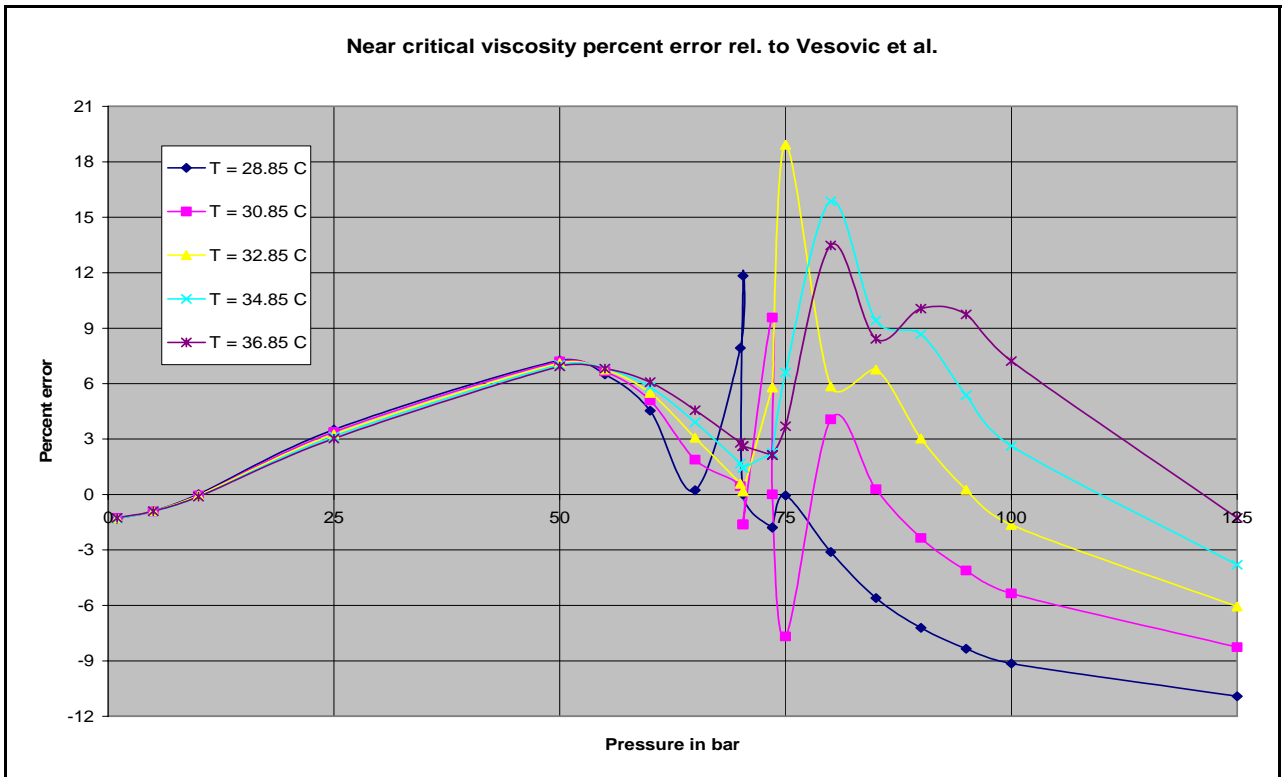


Fig. 3.2.3.9 CO₂ viscosity percent error near critical area

Some points from the graphs above:

- The increase of pressure at constant temperature always increases the viscosity while the increase of temperature at constant pressure may cause the viscosity to increase or decrease depends on what “fluid behave” at that state. If the initial state is in liquid phase or “seems more to be liquid than gas” then the increase of temperature causes the decrease of viscosity and the vice versa is valid which at gas phase, the increase of temperature increases the viscosity.
- Near critical area, the changes of pressure and/or temperature give the significant changes in viscosity. CO₂ viscosity at constant pressure changes rapidly due to the change of temperature below 200 °C and can be assumed linier above it.
- The saturated viscosity values predicted by correlations vary more at liquid phase than at gas phase. TOTAL correlations for saturated viscosity result in a bit overestimate on saturated liquid and underestimate on saturated gas but this correlation still can be used to estimate the saturated viscosity at the area a bit far from critical point.
- The comparison shows the consistency of the three correlations (Reichenberg, Vesovic and PVTsim) to estimate viscosity value. The trends are the same in all graphs and also the deviation is small. This suggests that we can use any of three methods presented above to estimate the viscosity in our area of interest even though at high temperature PVTsim and Reichenberg tends to overestimate.
- Below is the table of viscosity percent error in our area of interest and at the area near the critical point:

Method	Viscosity percent error		Viscosity percent error	
	Area of interest		Near critical area	
	Min.	Max.	Min.	Max.
Reichenberg	-8	8	-11	19
PVTsim	-8	10	-14	10

Table 3.2.3.1 CO₂ viscosity percent error

The table shows both of correlations estimate the viscosity in our area of interest with error less than 10 % and 20 % near critical area.

3.2.4.1 CO₂ Enthalpy-Pressure plot

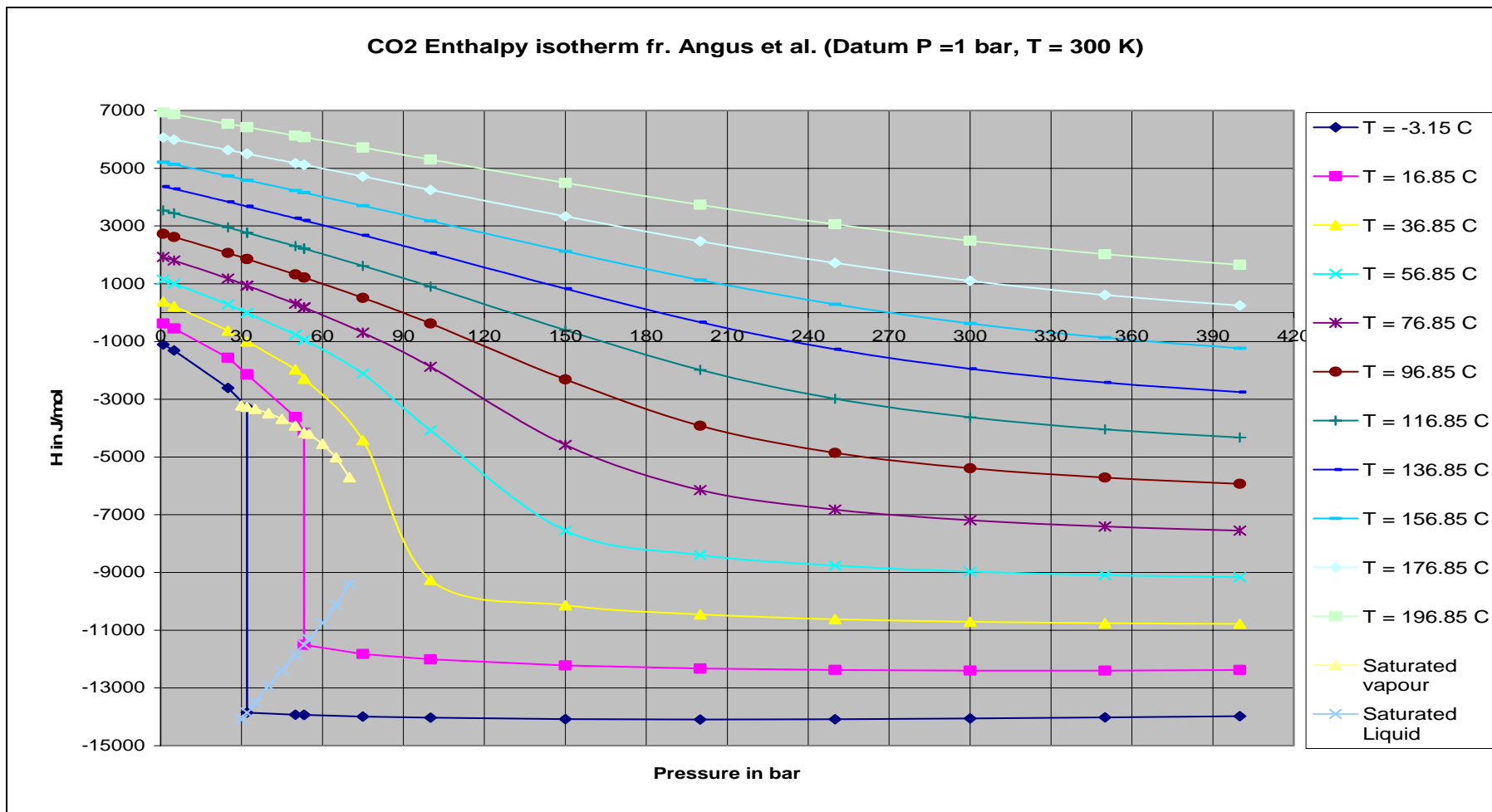


Fig. 3.2.4.1 CO₂ Enthalpy-Pressure plot for many isotherms (taken from Angus et al.)

3.2.4.2 Comparison of CO₂ Enthalpy

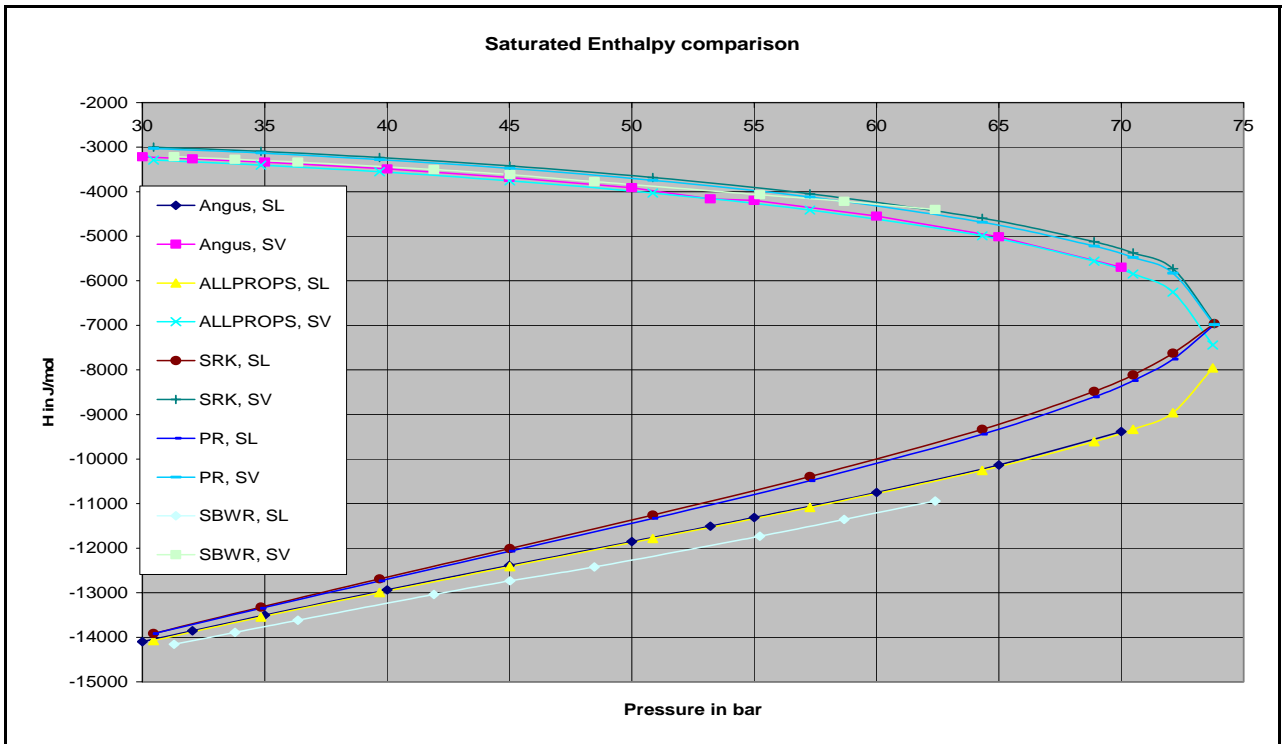


Fig. 3.2.4.2 Saturated CO₂ enthalpy comparison

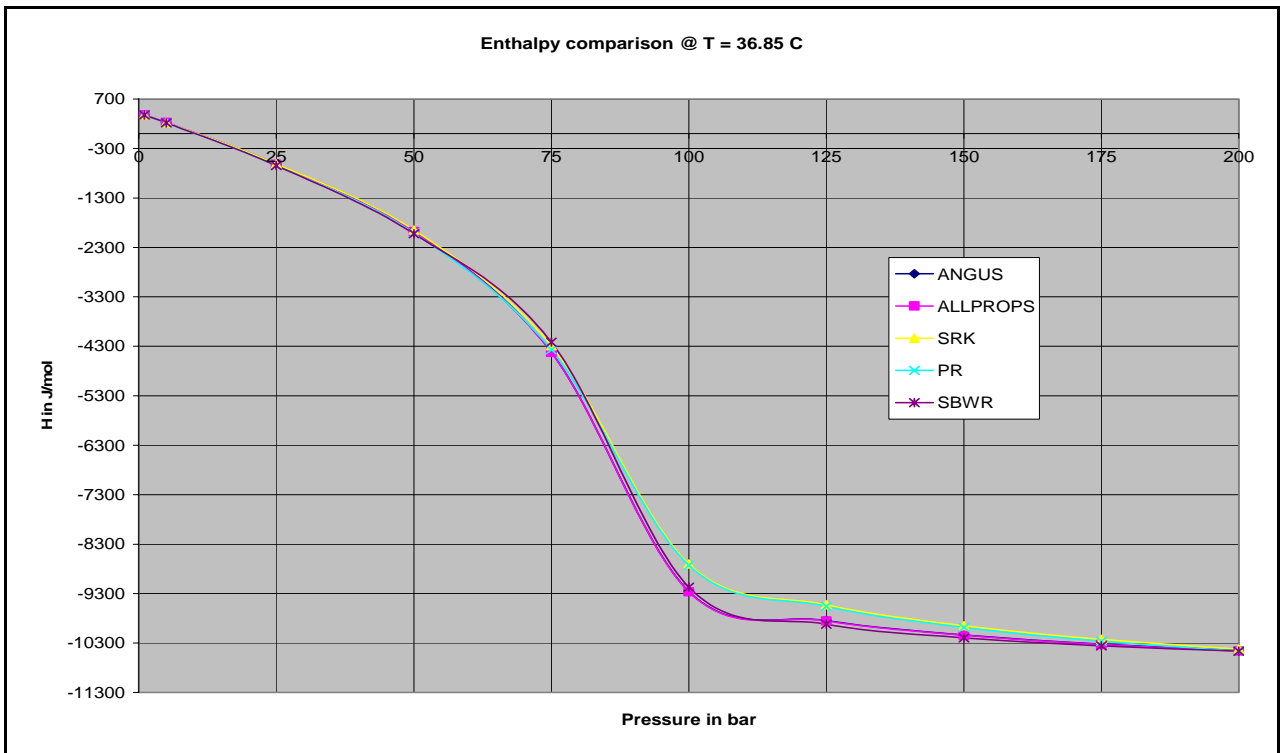


Fig. 3.2.4.3 CO₂ enthalpy comparison at T = 36.85 °C

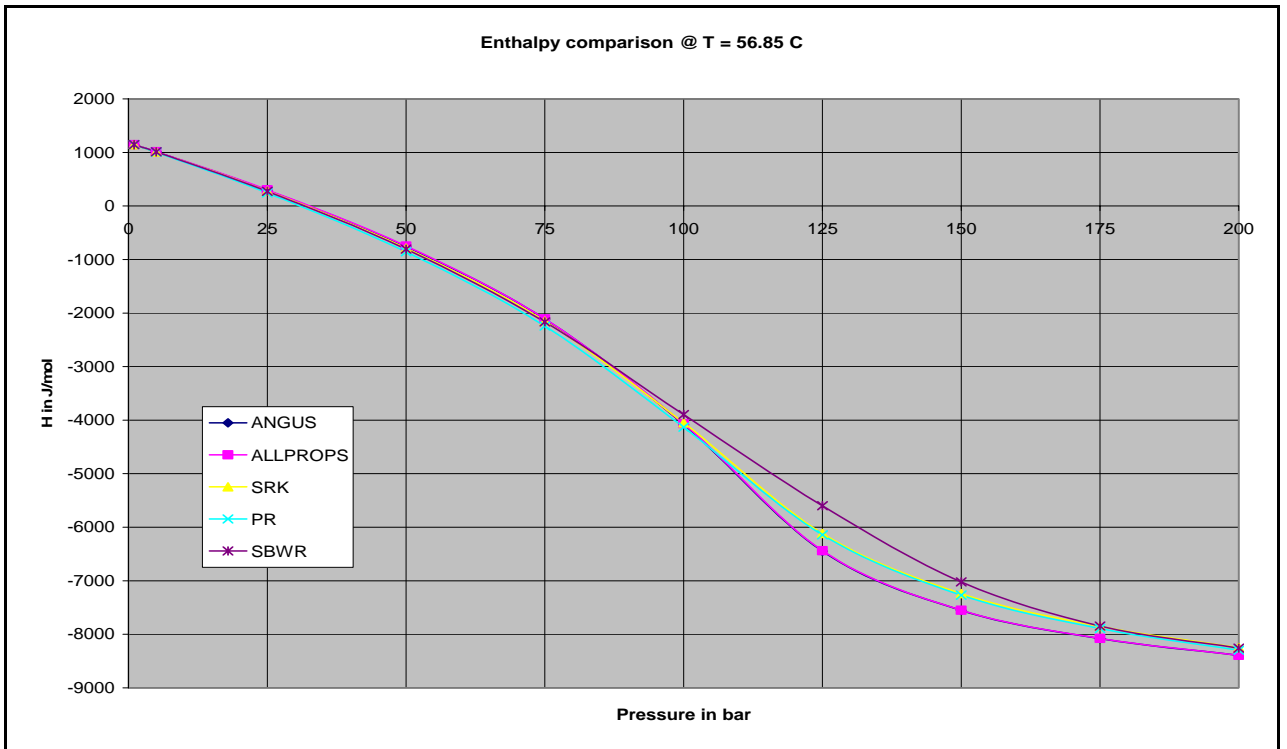


Fig. 3.2.4.4 CO₂ enthalpy comparison at T = 56.85 °C

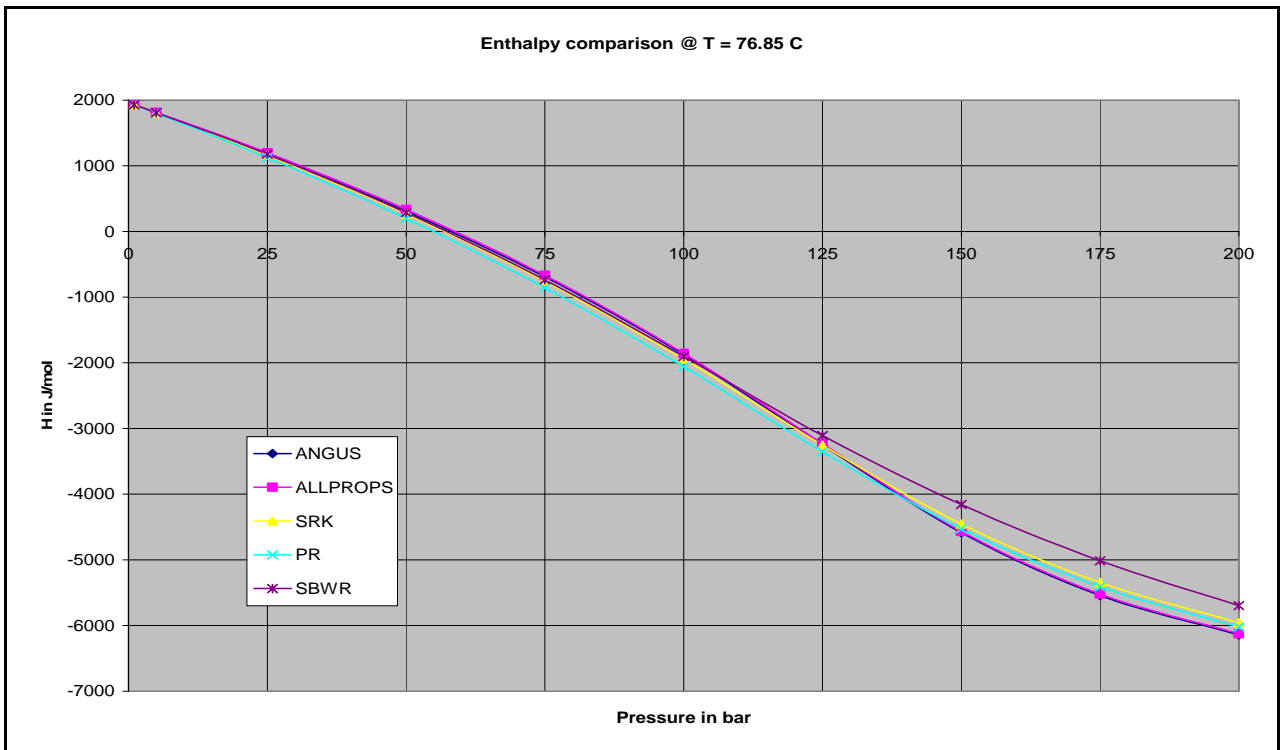


Fig. 3.2.4.5 CO₂ enthalpy comparison at T = 76.85 °C

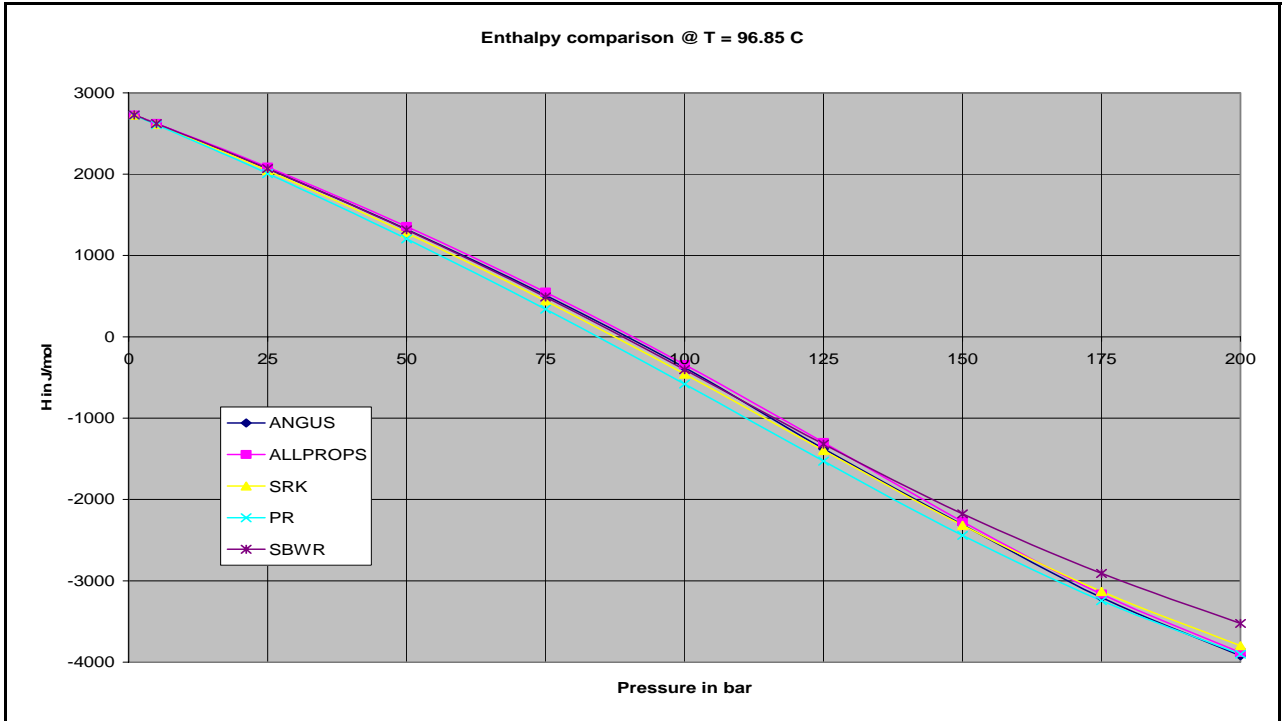


Fig. 3.2.4.6 CO₂ enthalpy comparison at T = 96.85 °C

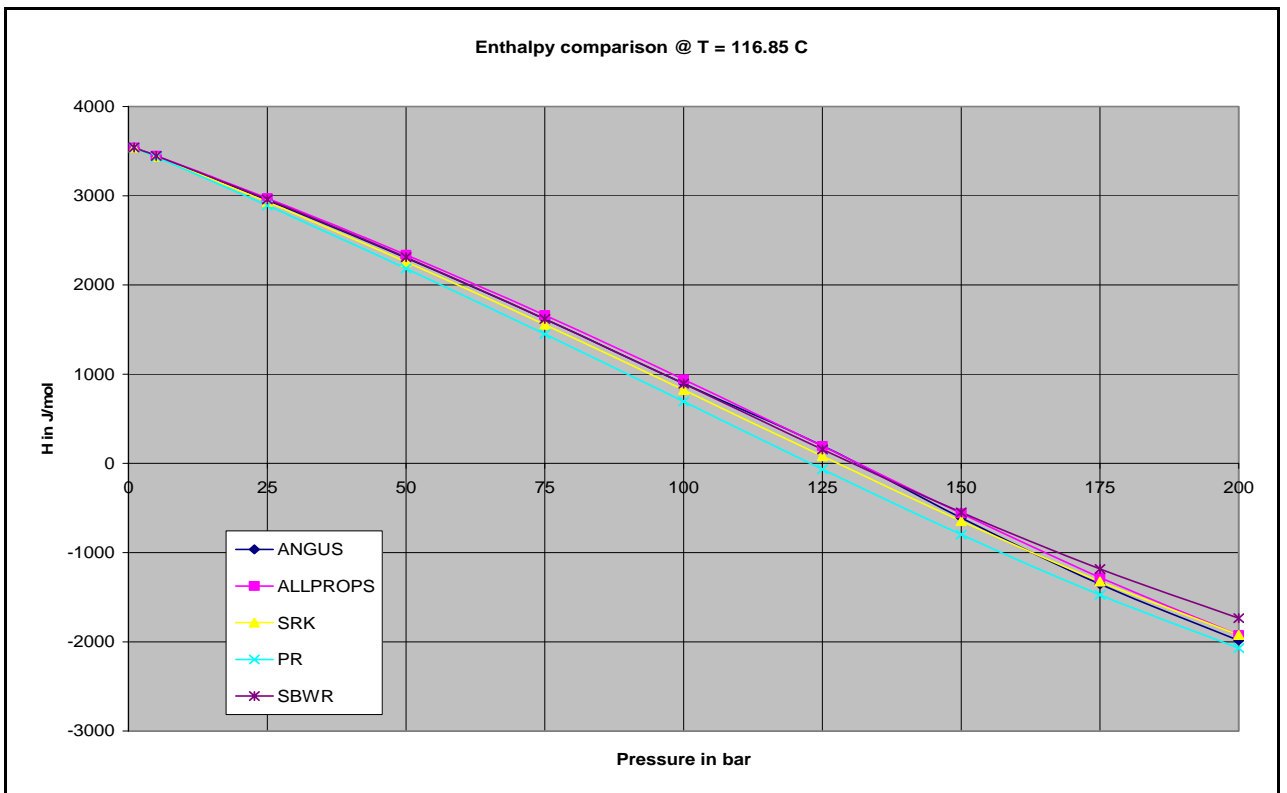


Fig. 3.2.4.7 CO₂ enthalpy comparison at T = 116.85 °C

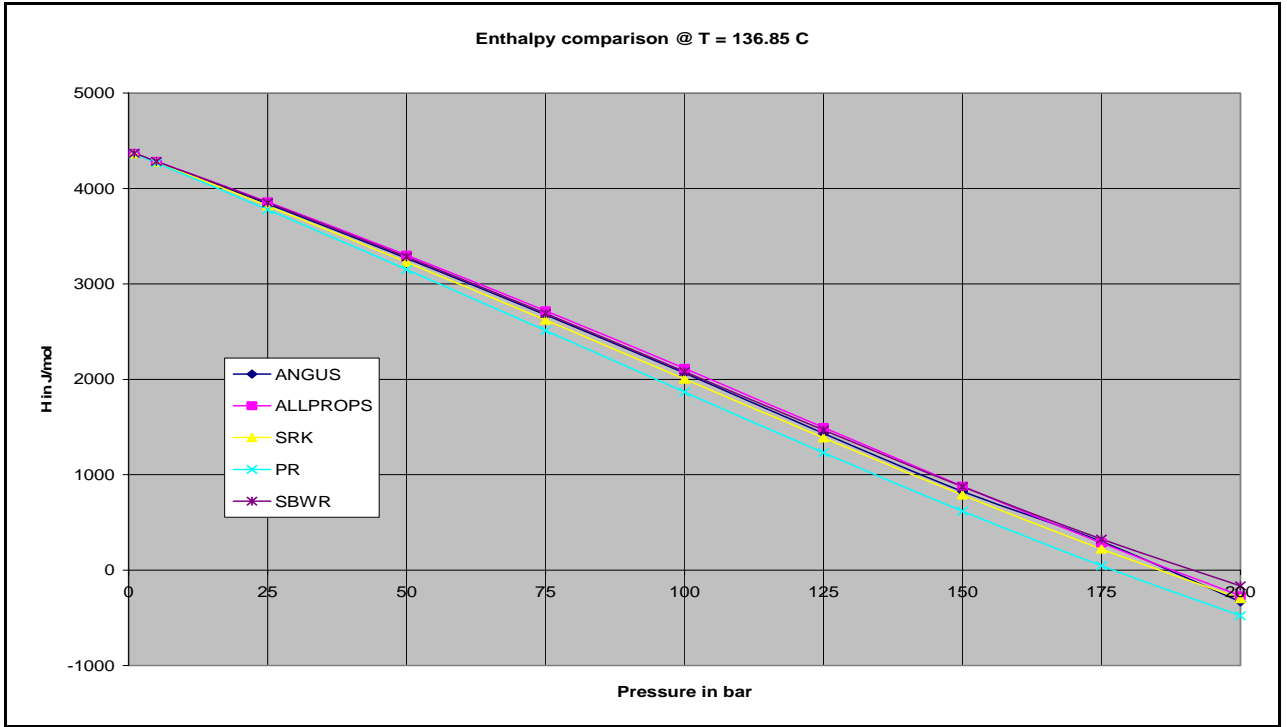


Fig. 3.2.4.8 CO₂ enthalpy comparison at T = 136.85 °C

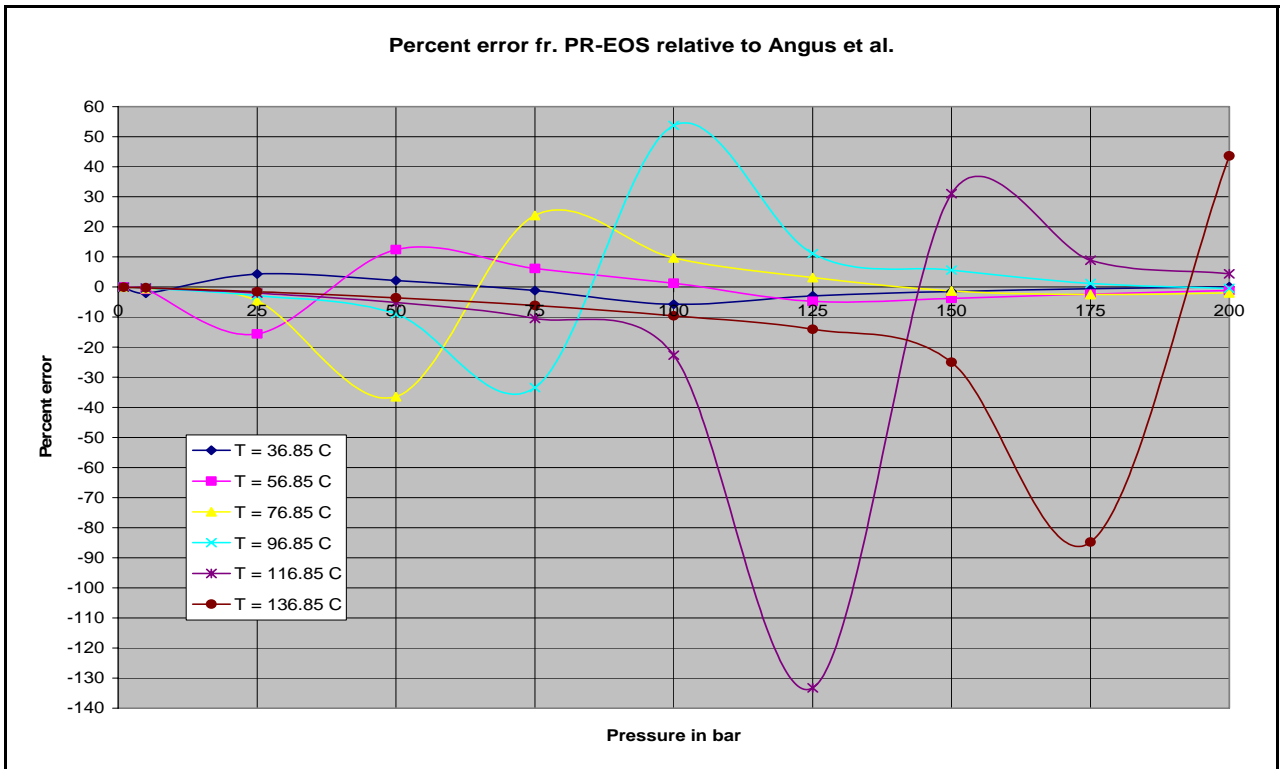


Fig. 3.2.4.9 CO₂ enthalpy percent error at area of interest from Peng-Robinson EOS

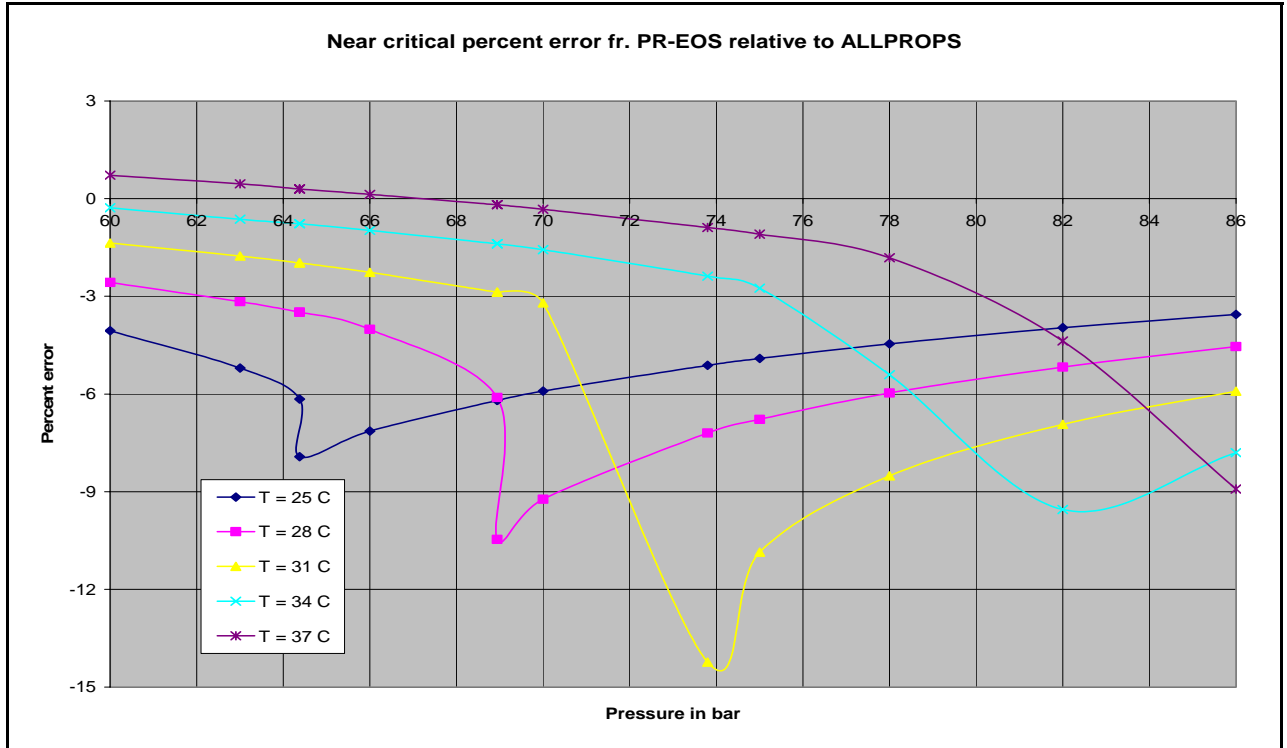


Fig. 3.2.4.10 CO₂ enthalpy percent error near critical area from Peng-Robinson EOS

Some important points regarding enthalpy from graphs above:

- The increase of temperature at constant pressure always causes the increase of enthalpy. For gas phase and at the state where the fluid behaves like the gas, the pressure increase causes the decrease of enthalpy while for liquid or the state of “liquid like” behavior, the increase of pressure causes the enthalpy to increase insignificantly and can be assumed constant (except near the liquid saturated point).
- The saturation lines position for enthalpy are different with density. In density, liquid saturation line is in the top, gas in the bottom and they meet at critical point. In enthalpy, liquid saturation line is in the bottom, gas in the top and they meet at critical point. The same thing is that the variation of enthalpy values predicted by correlation is larger at saturated liquid than saturated vapor. It means uncertainty in saturated liquid is higher than saturated gas.

- Every equation of state used in this work shows the same trend, only SBWR tends to overestimate at high pressure. Also, at high pressure the uncertainty of enthalpy value predicted by EOS is getting larger due to the more varying enthalpy values predicted for the same state.
- Below is the table that shows the enthalpy percent error for the area of interest and for near critical region:

Method	Enthalpy percent error		Enthalpy percent error	
	Area of interest		Near critical area	
	Min.	Max.	Min.	Max.
Peng-Robinson	-133	54	-14	1
Starling-BWR	-50	9	-42	6
Soave-Redlich-Kwong	-59	21	-15	-2
ALLPROPS	-19	9		

Table 3.2.4.1 CO₂ Enthalpy percent error

- From the table we observe that even for ALLPROPS that estimate very well on density, has quite large error until 20 %. Cubic equation state usually underestimate the value of enthalpy up to 60% and the worst is PR-EOS which up to 135 %. Enthalpy is calculated using two departure functions and one ideal difference function. Each has their own error and the “accumulation” of error is alleged as the cause of the large error in enthalpy value estimation

3.2.5.1 CO₂ Internal Energy-Pressure plot

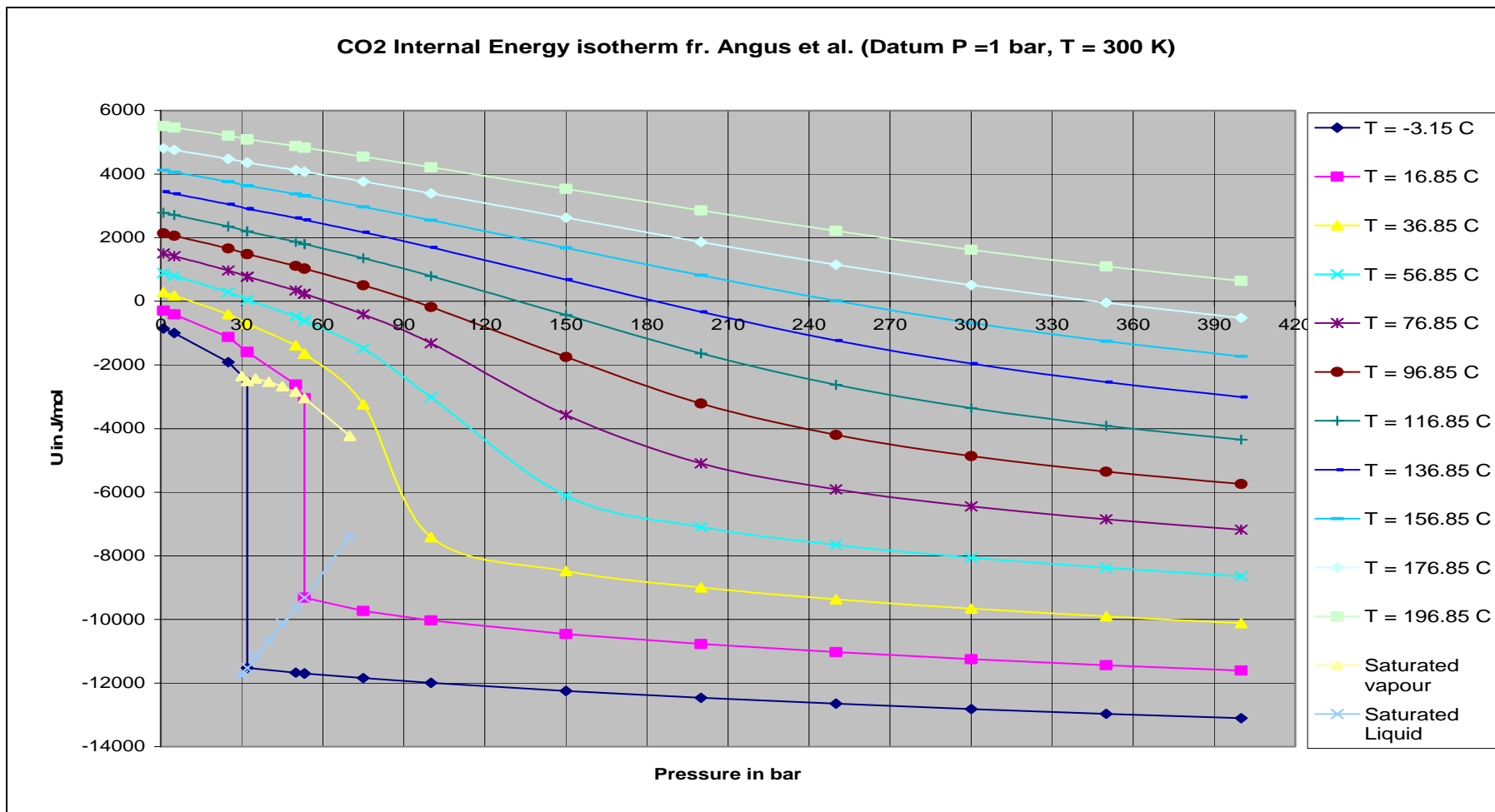


Fig. 3.2.5.1 CO₂ Internal Energy-Pressure plot for many isotherms (taken from Angus et al.)

3.2.5.2 Comparison of CO₂ Internal Energy

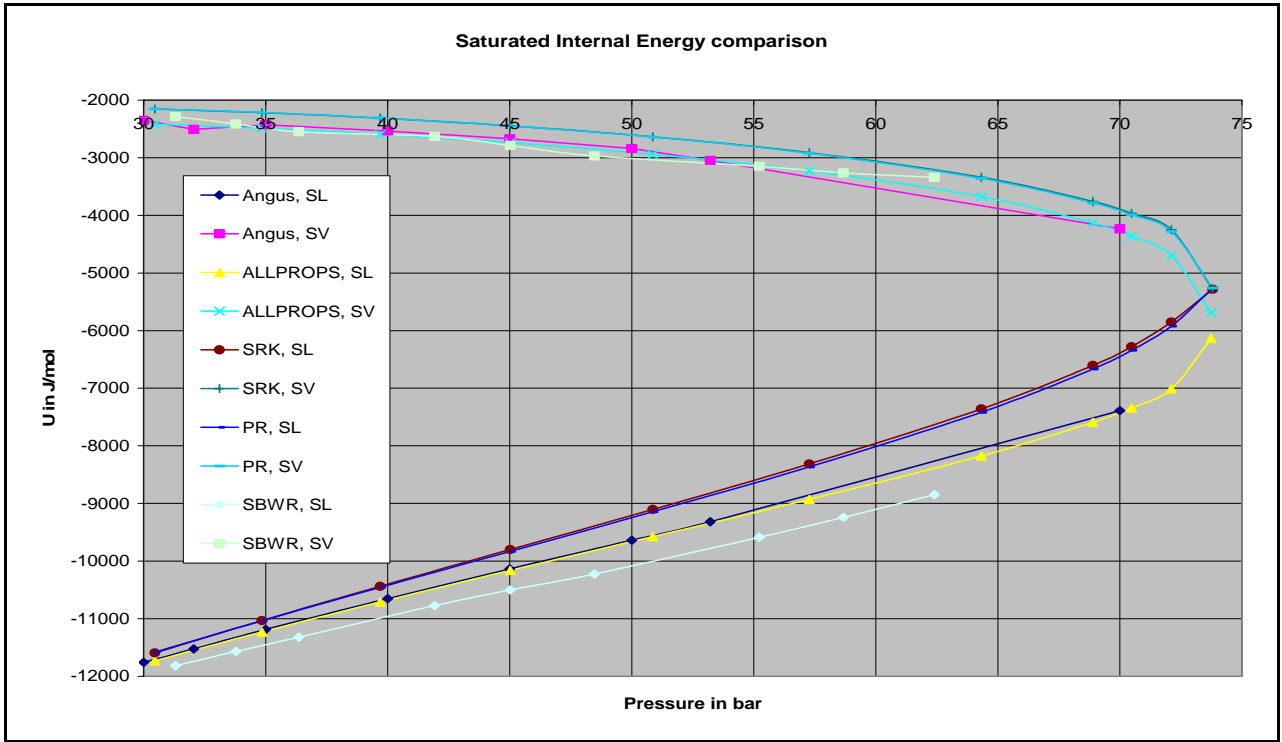


Fig. 3.2.5.2 Saturated CO₂ Internal Energy comparison

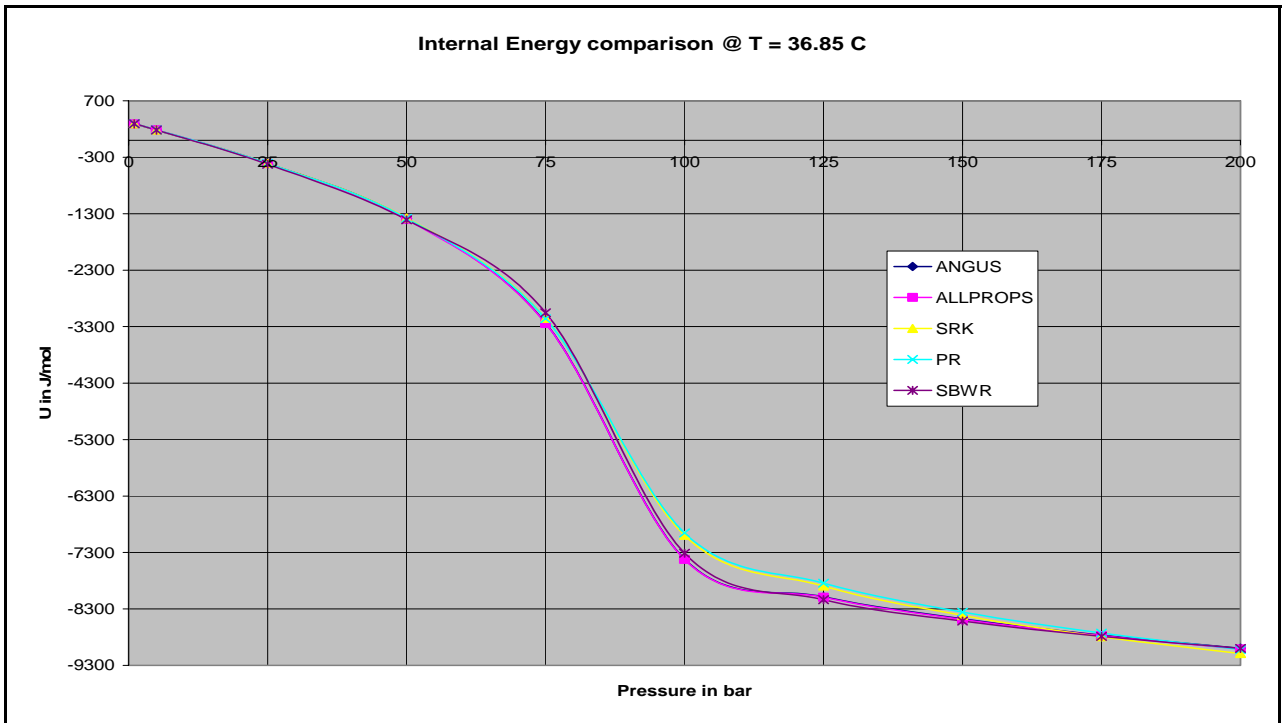


Fig 3.2.5.3 CO₂ Internal energy comparison at T = 36.85 °C

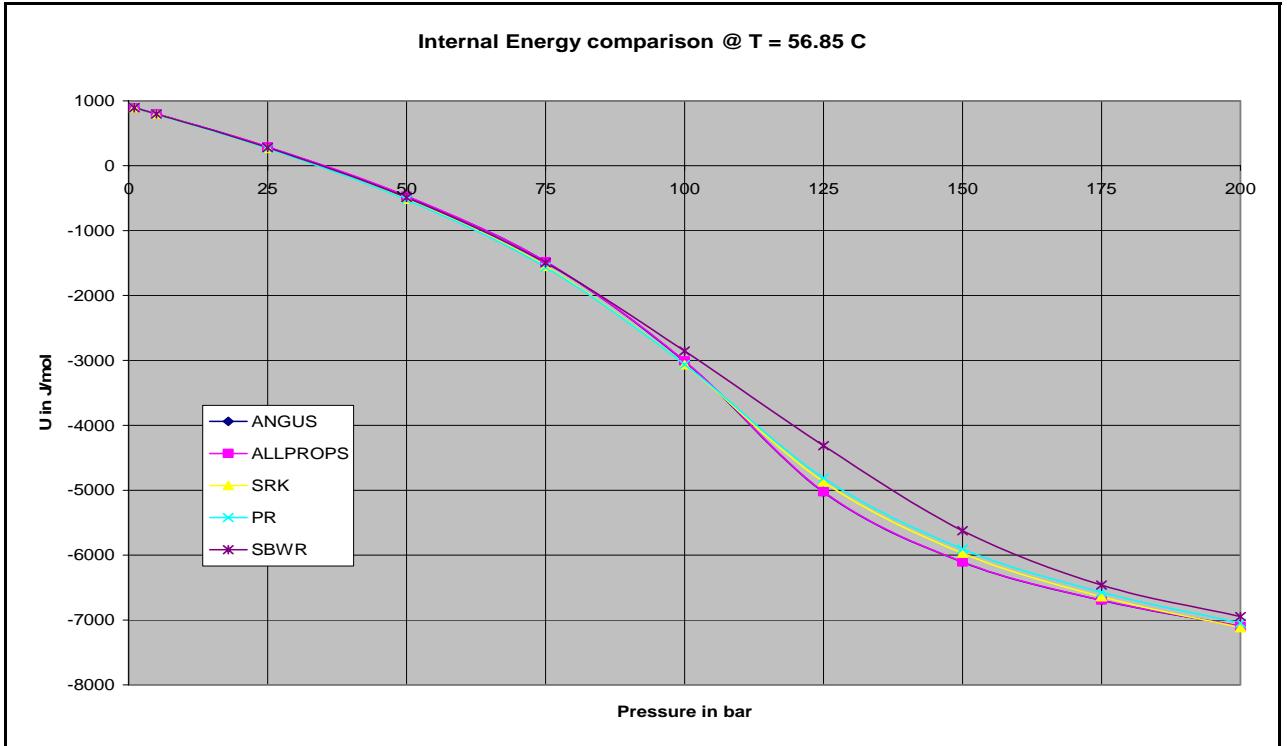


Fig 3.2.5.4 CO₂ Internal energy comparison at T = 56.85 °C

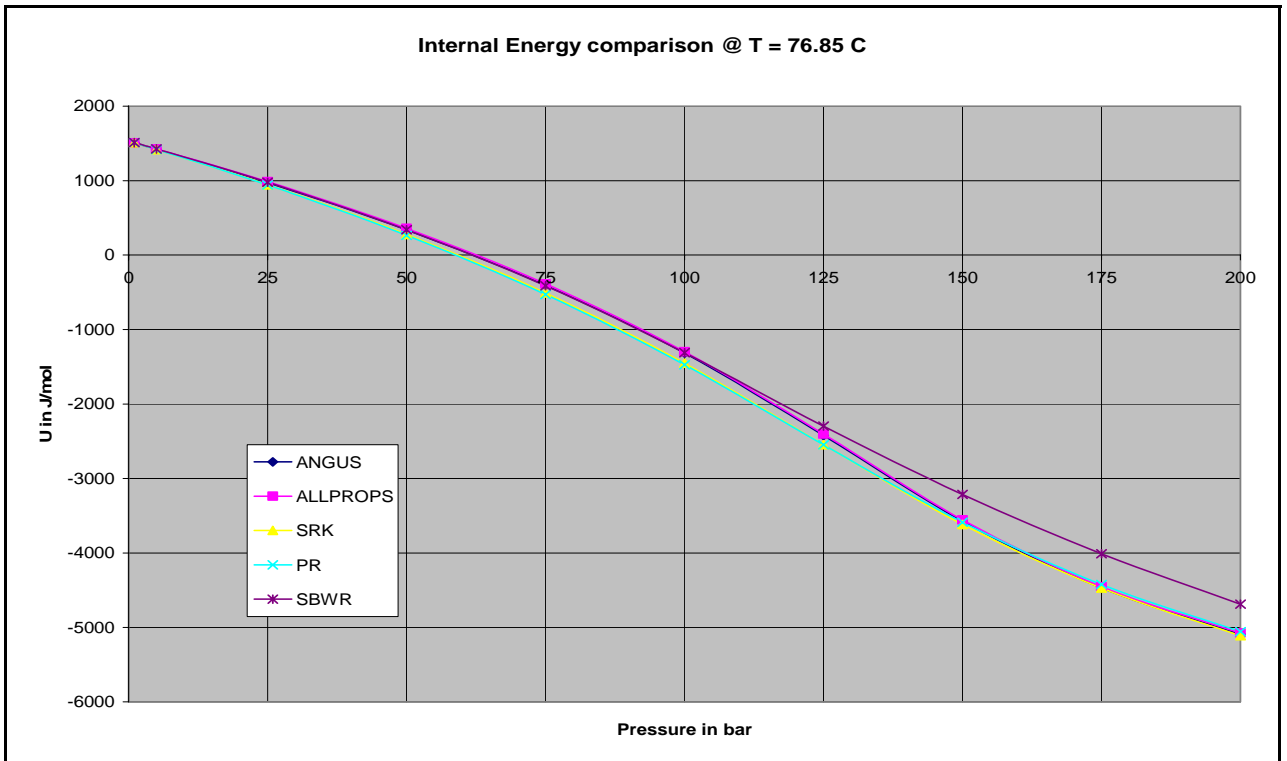
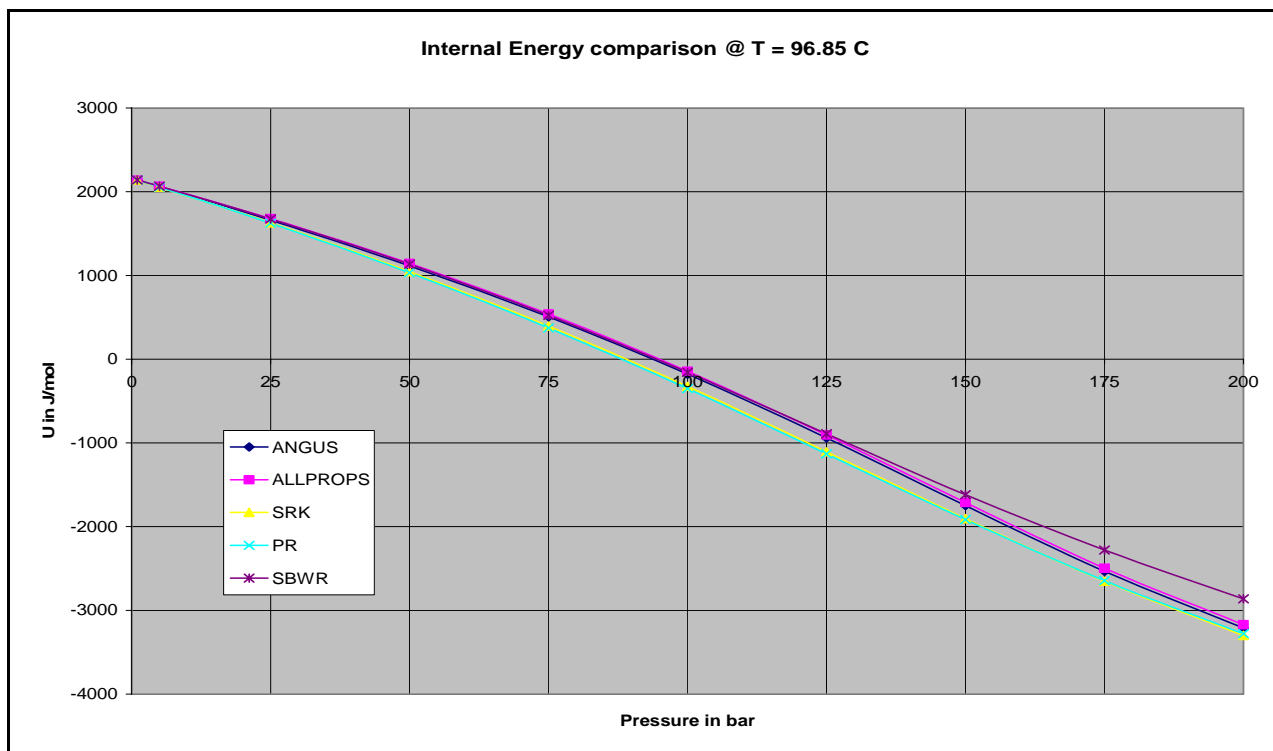
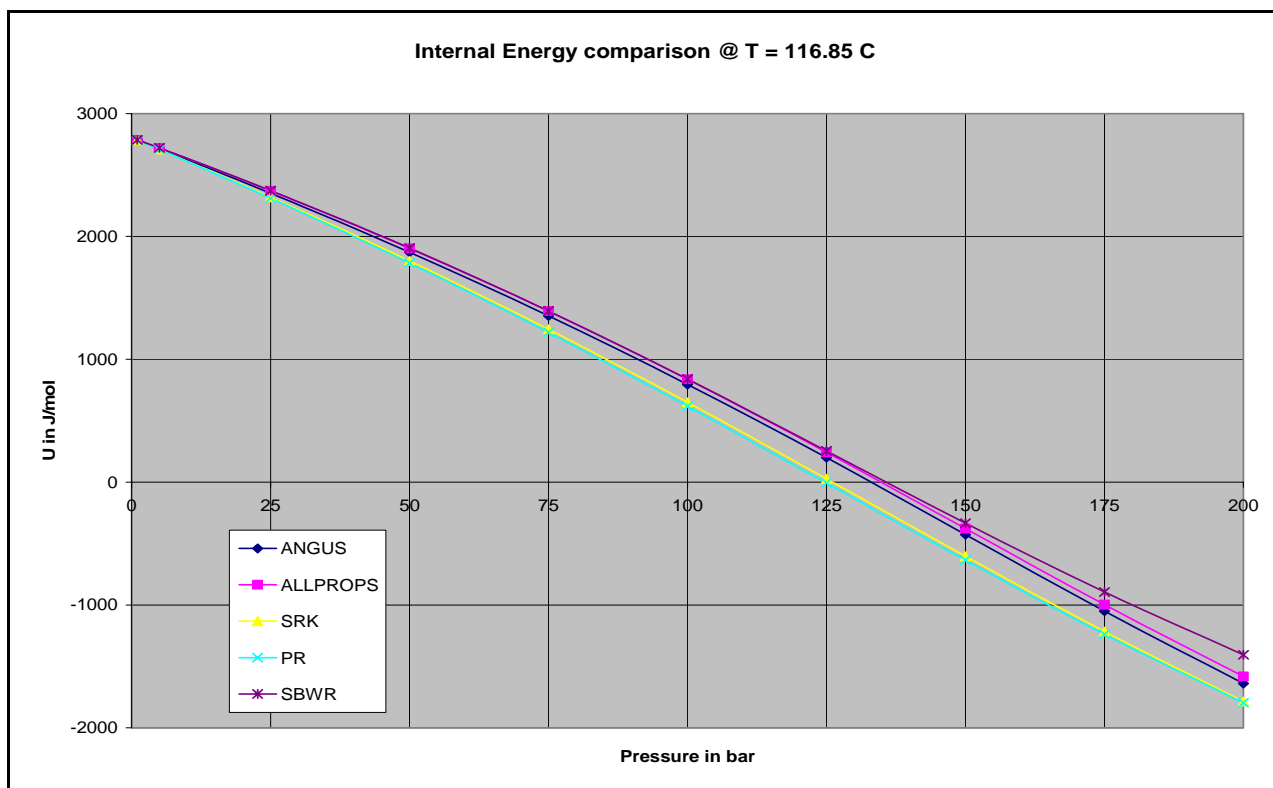


Fig 3.2.5.5 CO₂ Internal energy comparison at T = 76.85 °C

Fig 3.2.5.6 CO₂ Internal energy comparison at T = 96.85 °CFig 3.2.5.7 CO₂ Internal energy comparison at T = 116.85 °C

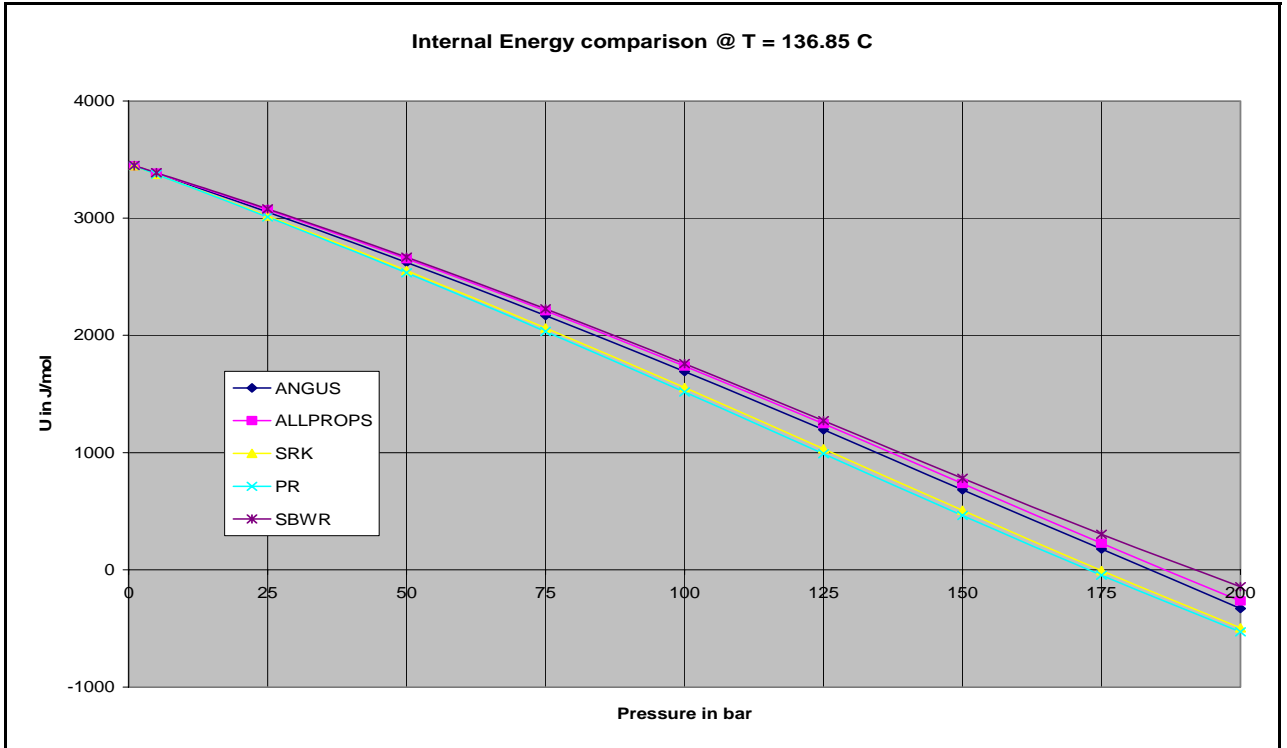


Fig 3.2.5.8 CO₂ Internal energy comparison at T = 136.85 °C

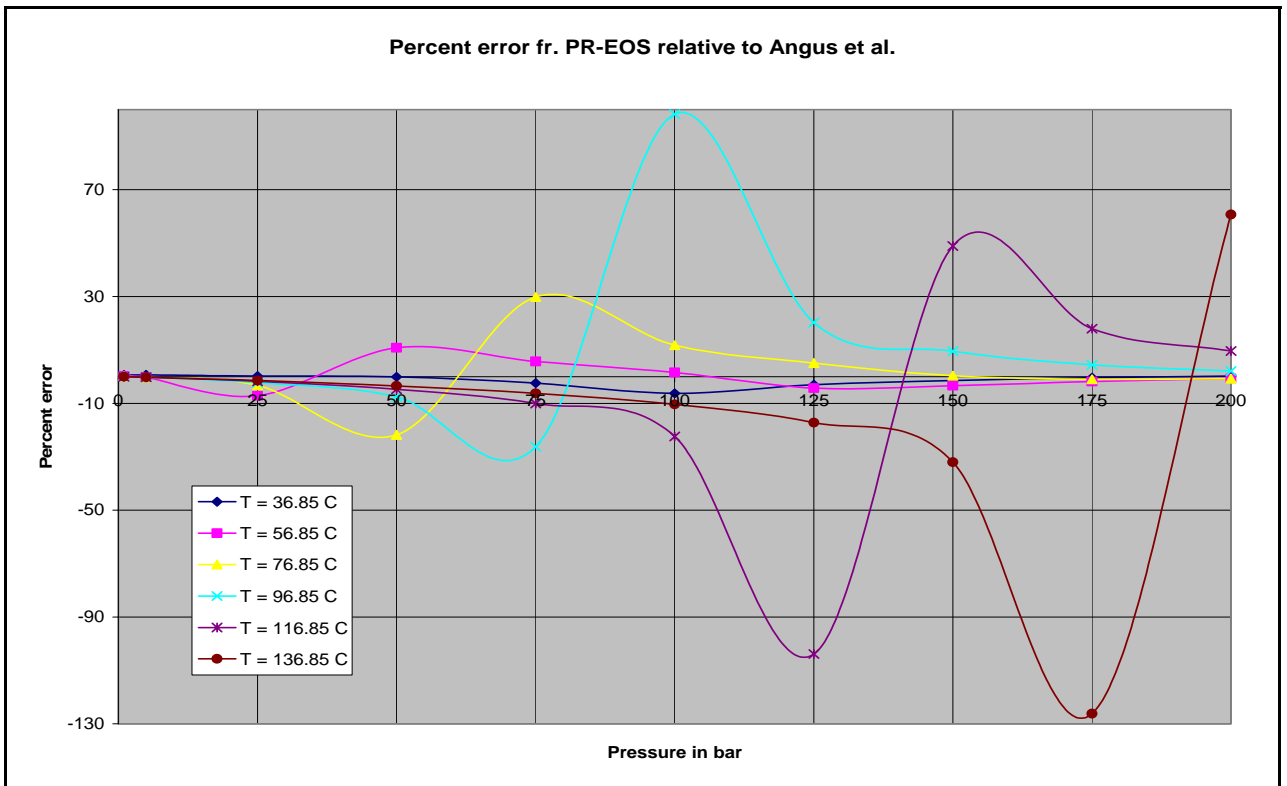


Fig. 3.2.5.9 CO₂ Internal energy percent error at area of interest from PR-EOS

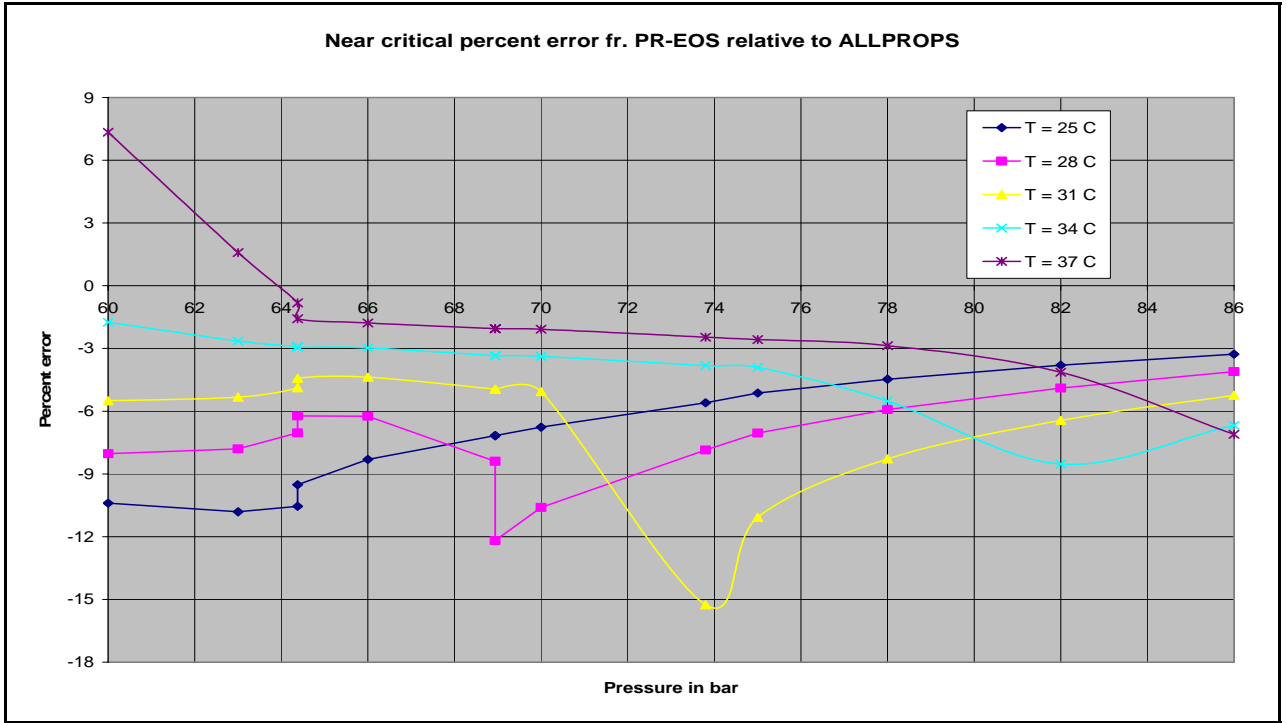


Fig. 3.2.5.10 CO₂ Internal energy percent error near critical area from PR-EOS

We notice that every graph in this section is the same with enthalpy section only different in the value. The different between enthalpy and internal energy is the flow work term. It is the product between pressure and specific volume of fluid. Because both of them are positive then the value of internal energy is always lower than enthalpy.

The discussion of internal energy is the same with enthalpy. Here we only present the table of internal energy percent error in our area of interest and near critical zone:

Method	Int. Energy percent error		Int. Energy percent error	
	Area of interest		Near critical area	
	Min.	Max.	Min.	Max.
Peng-Robinson	-133	99	-16	8
Starling-BWR	-60	71	-39	9
Soave-Redlich-Kwong	-104	83	-24	0
ALLPROPS	-20	30		

Table 3.2.5.1 CO₂ Internal Energy percent error

The error table shows that the percent error of internal energy even worst than enthalpy. It is because internal energy is obtained from enthalpy by subtracting the enthalpy with the flow work term. This term automatically contains error from the side of specific volume. So, again the “error addition” happens. This could be the explanation why the percent error getting higher compared to enthalpy percent error.

The irony is that in near critical area enthalpy and internal energy show much better percent error compared to the percent error in our area of interest. Density, viscosity, and other properties show the different pattern where the highest error happens in near critical area. To answer this problem, more researches in this particular case are needed and would not be the subject in this work.

3.2.6.1 CO₂ Entropy-Pressure plot

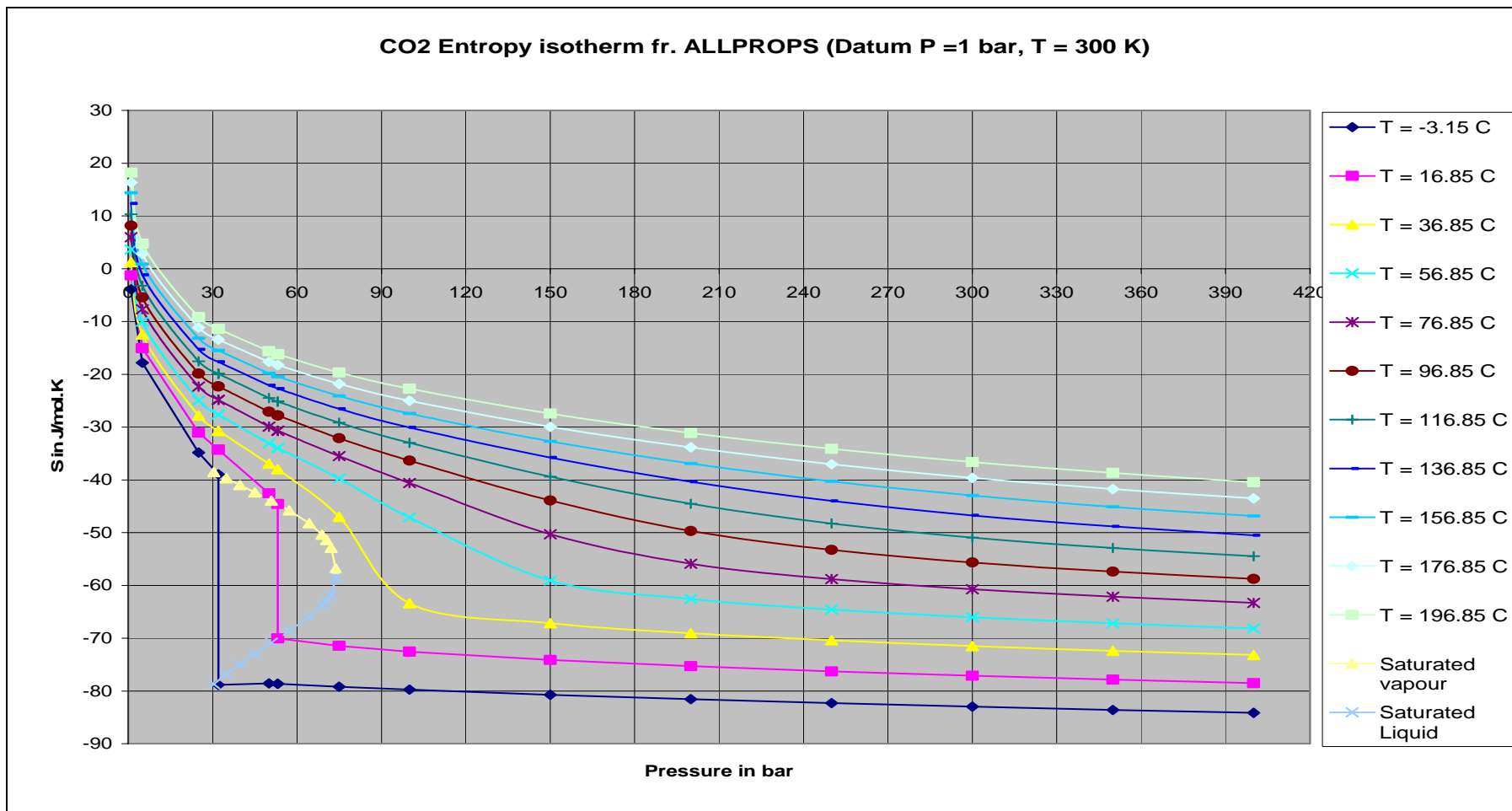


Fig. 3.2.6.1 CO₂ Entropy-Pressure plot for many isotherms (obtained from ALLPROPS)

3.2.6.2 Comparison of CO₂ Entropy

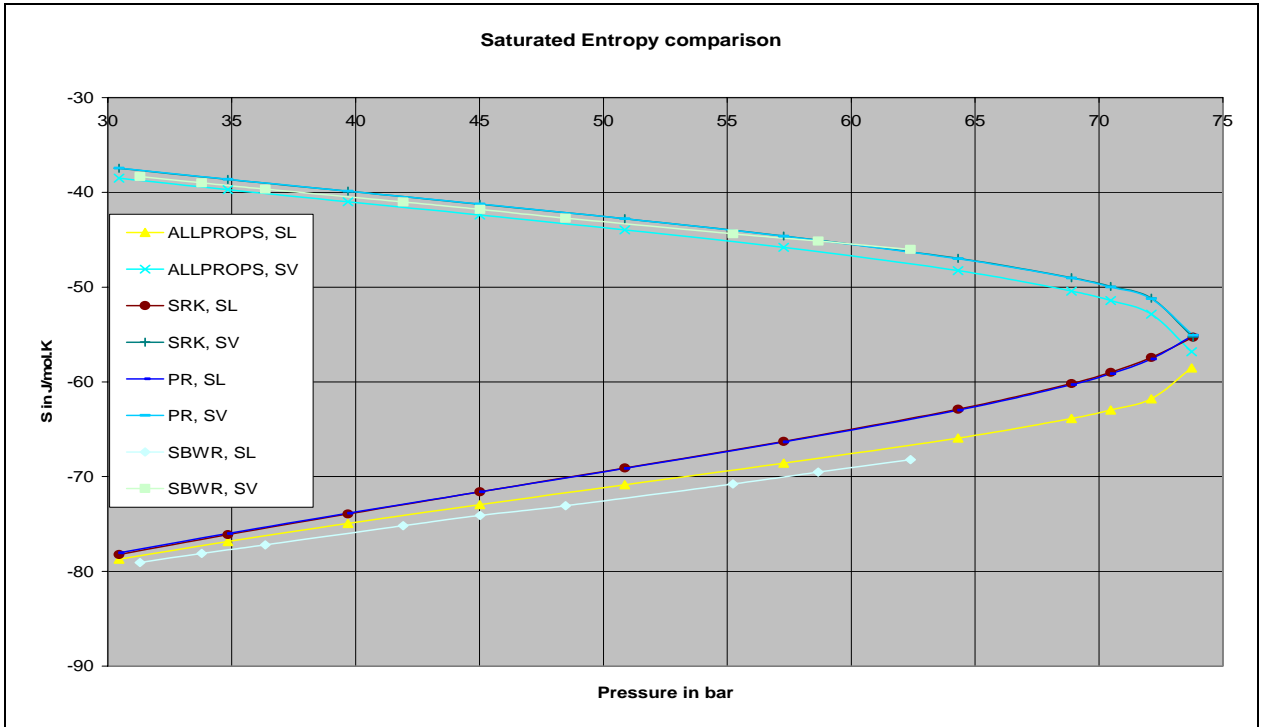


Fig. 3.2.6.2 Saturated CO₂ Entropy comparison

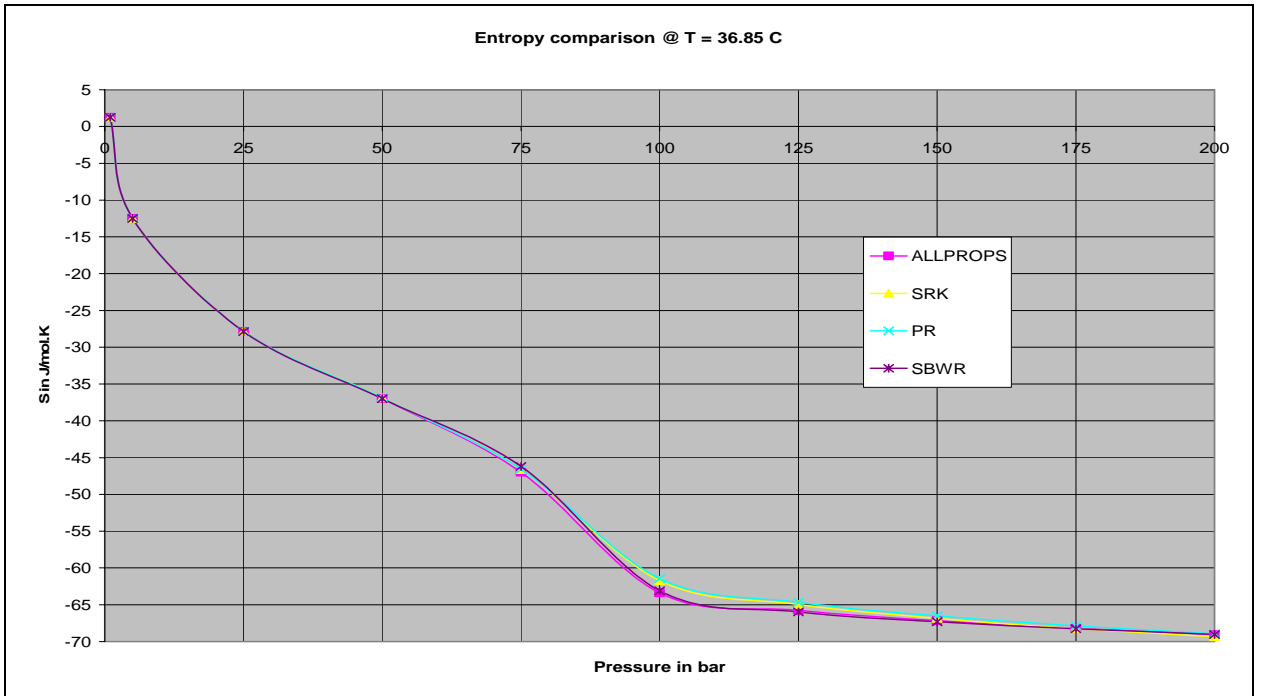


Fig 3.2.6.3 CO₂ Entropy comparison at T = 36.85 °C

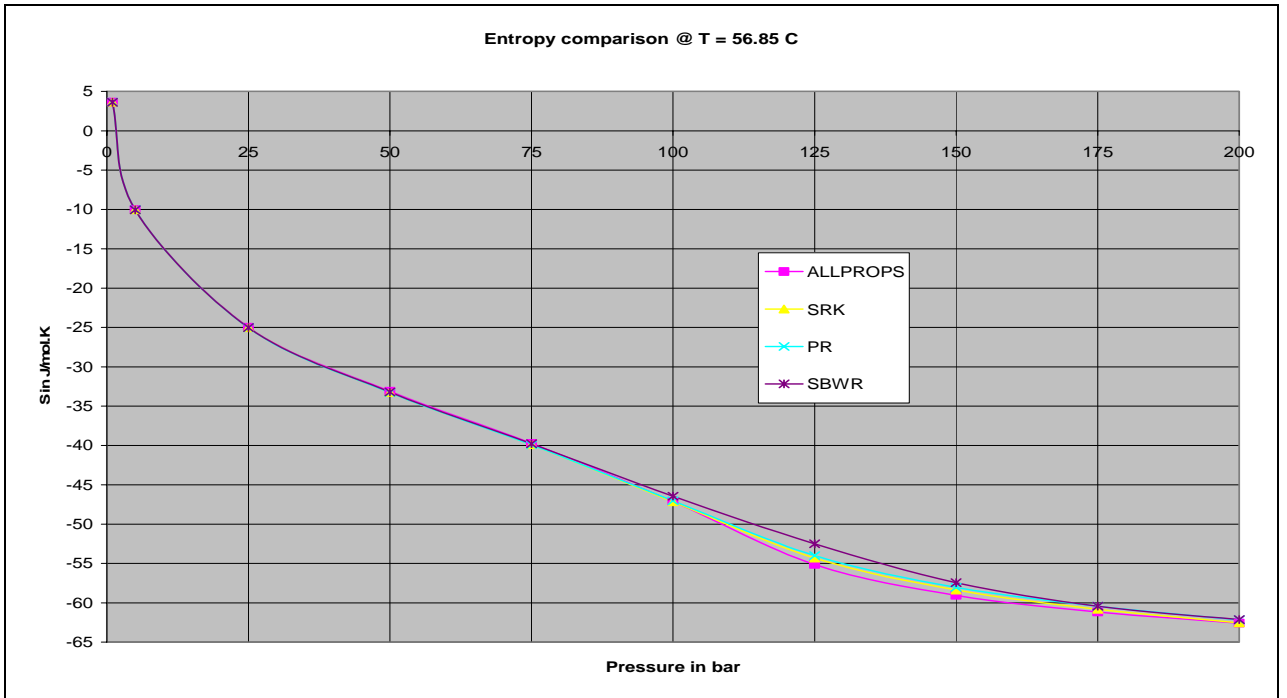


Fig 3.2.6.4 CO₂ Entropy comparison at T = 56.85 °C

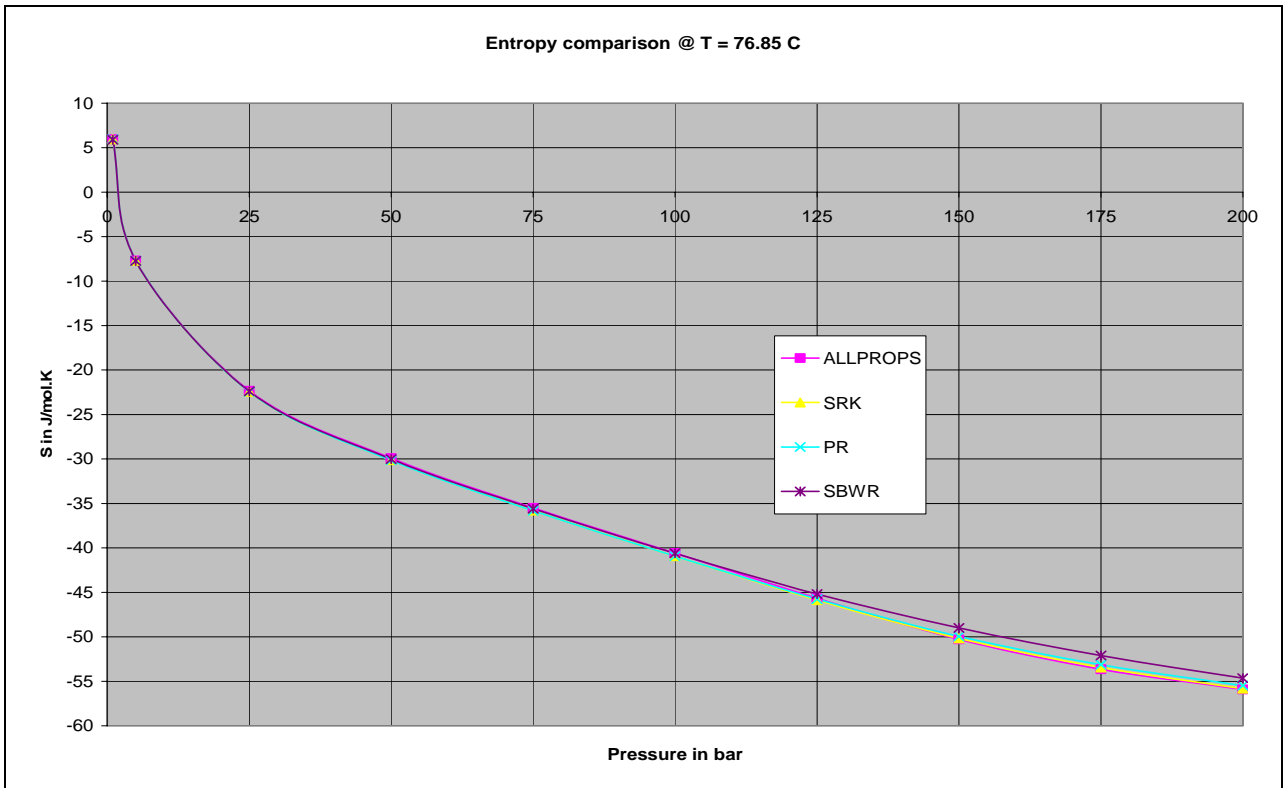


Fig 3.2.6.5 CO₂ Entropy comparison at T = 76.85 °C

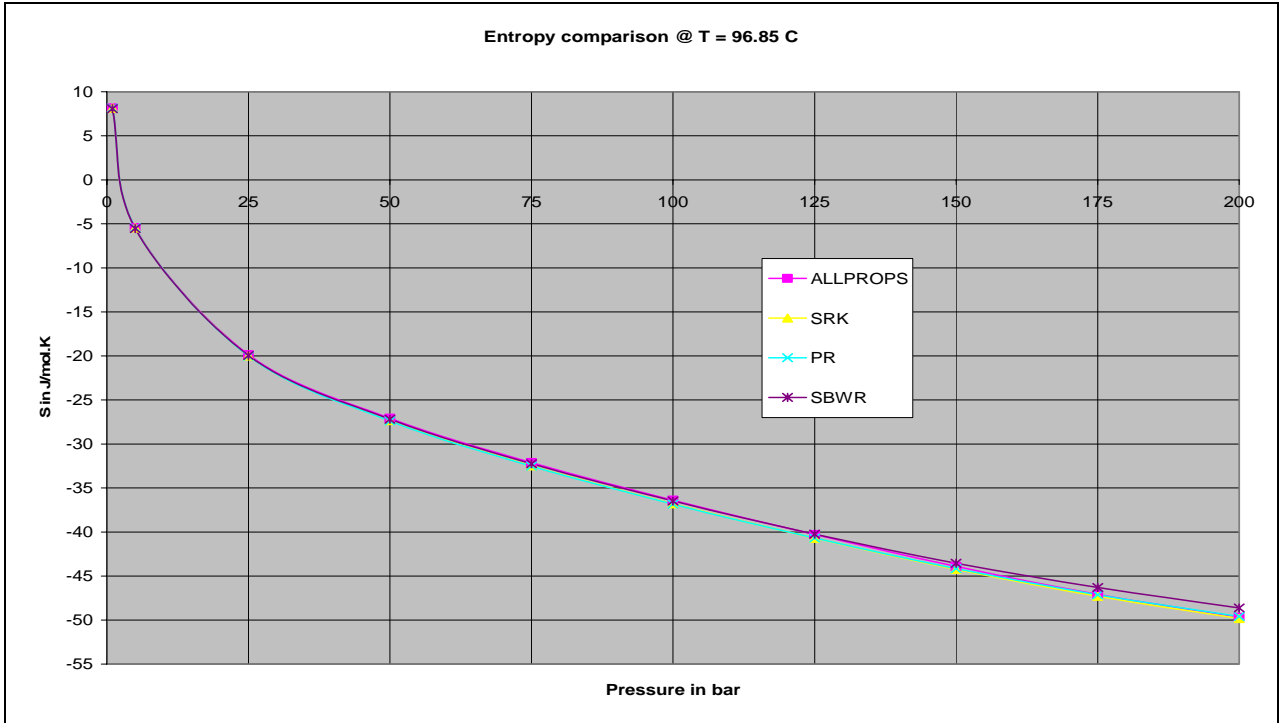


Fig 3.2.6.6 CO₂ Entropy comparison at T = 96.85 °C

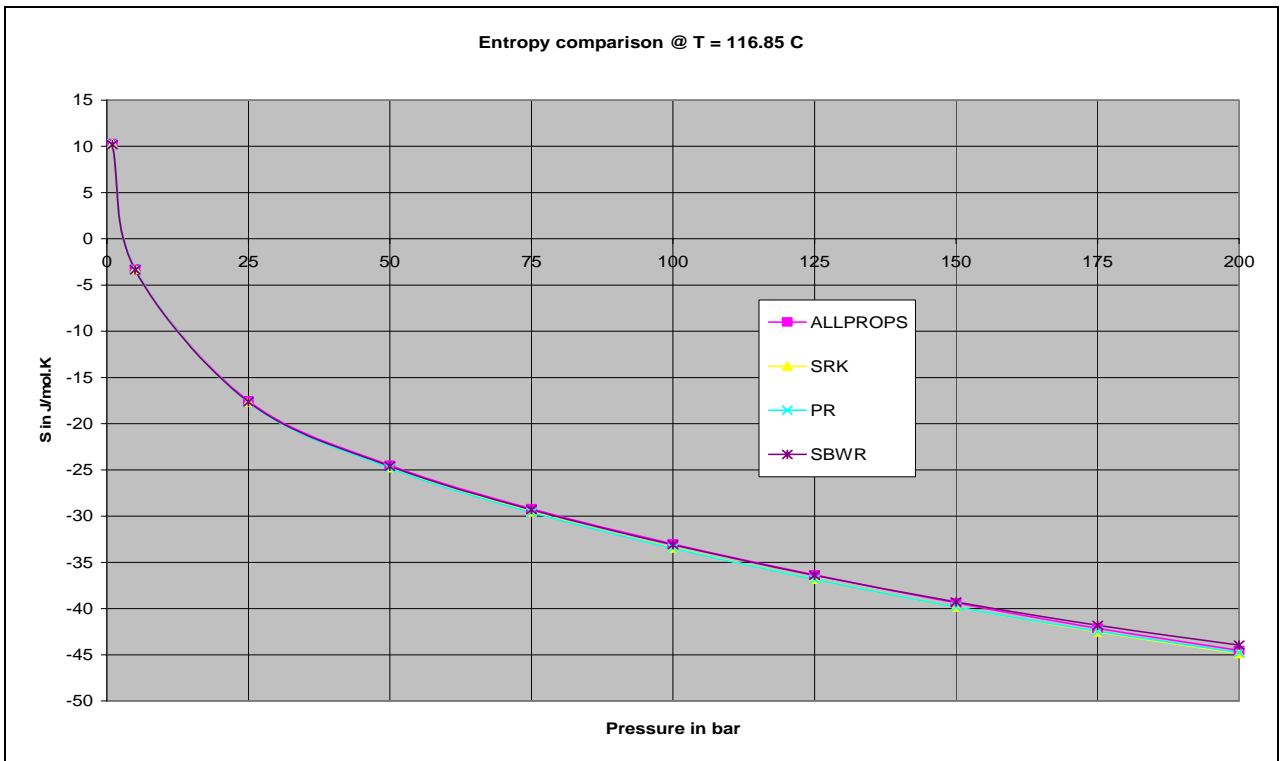


Fig 3.2.6.7 CO₂ Entropy comparison at T = 116.85 °C

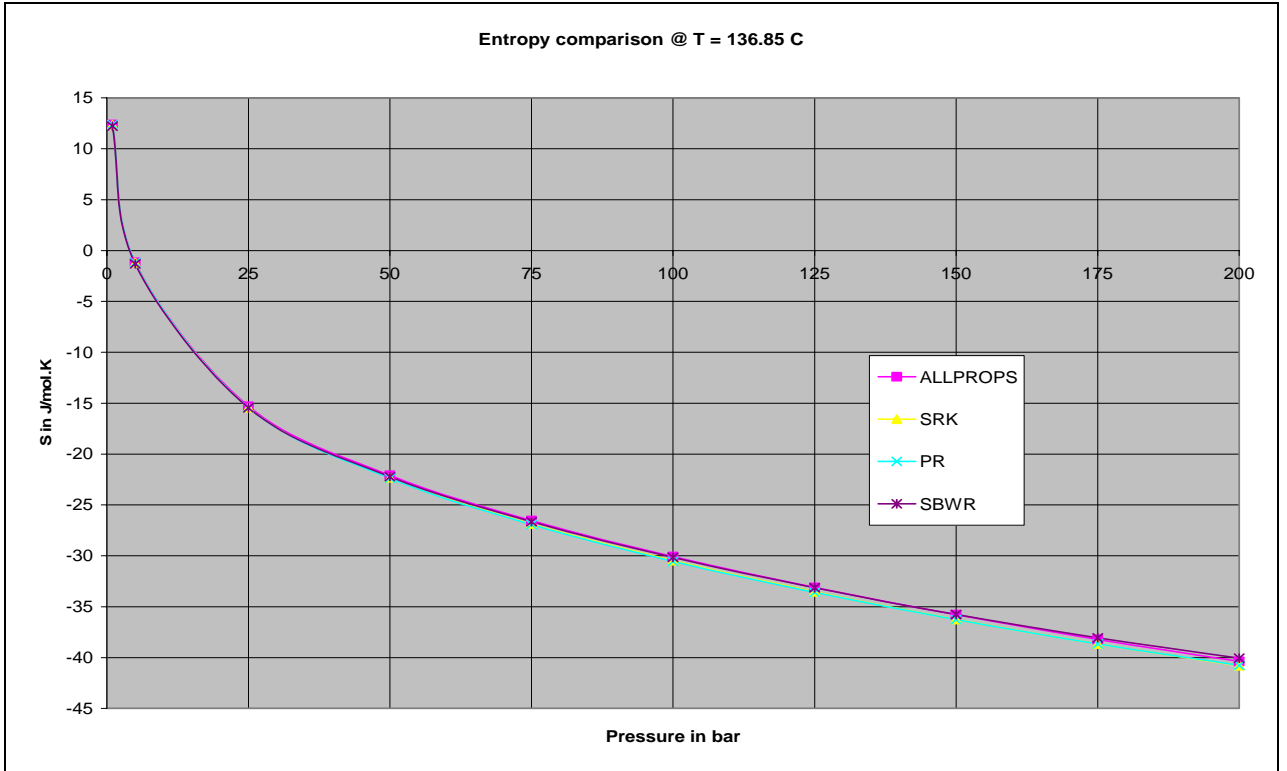


Fig 3.2.6.8 CO₂ Entropy comparison at T = 136.85 °C

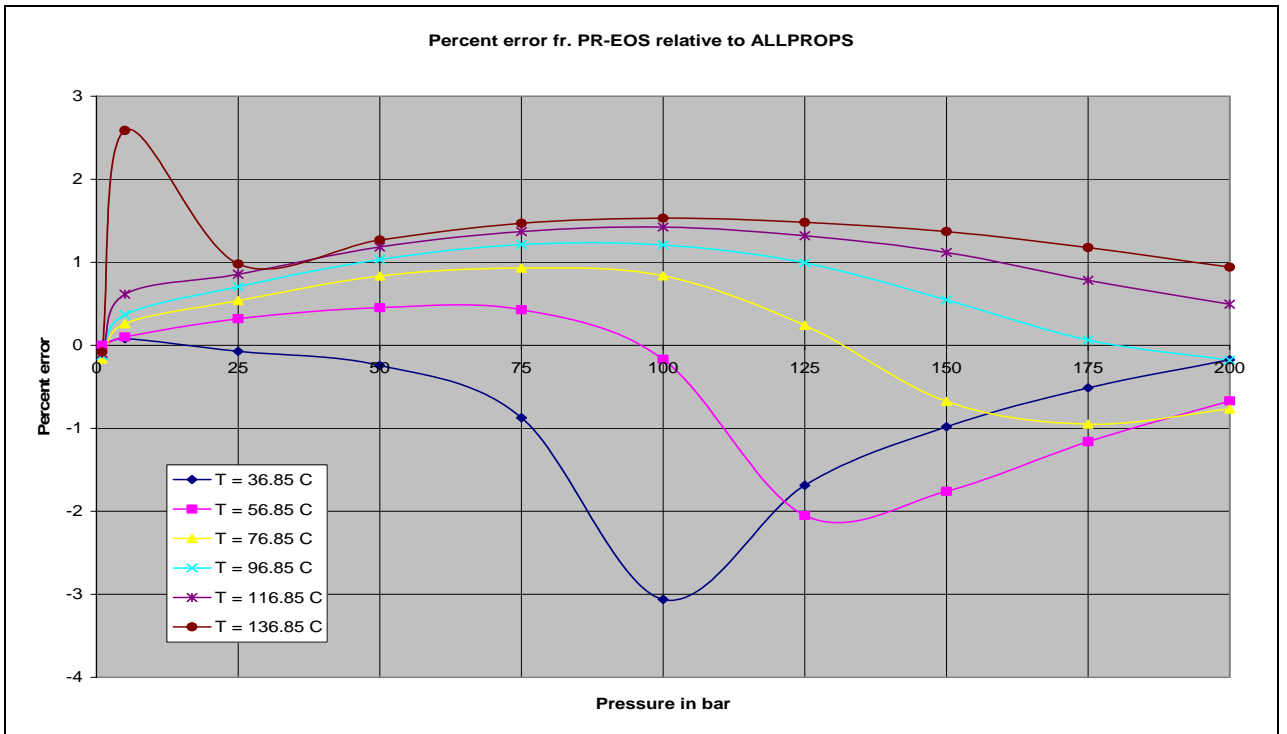


Fig. 3.2.6.9 CO₂ Entropy percent error at area of interest from PR-EOS

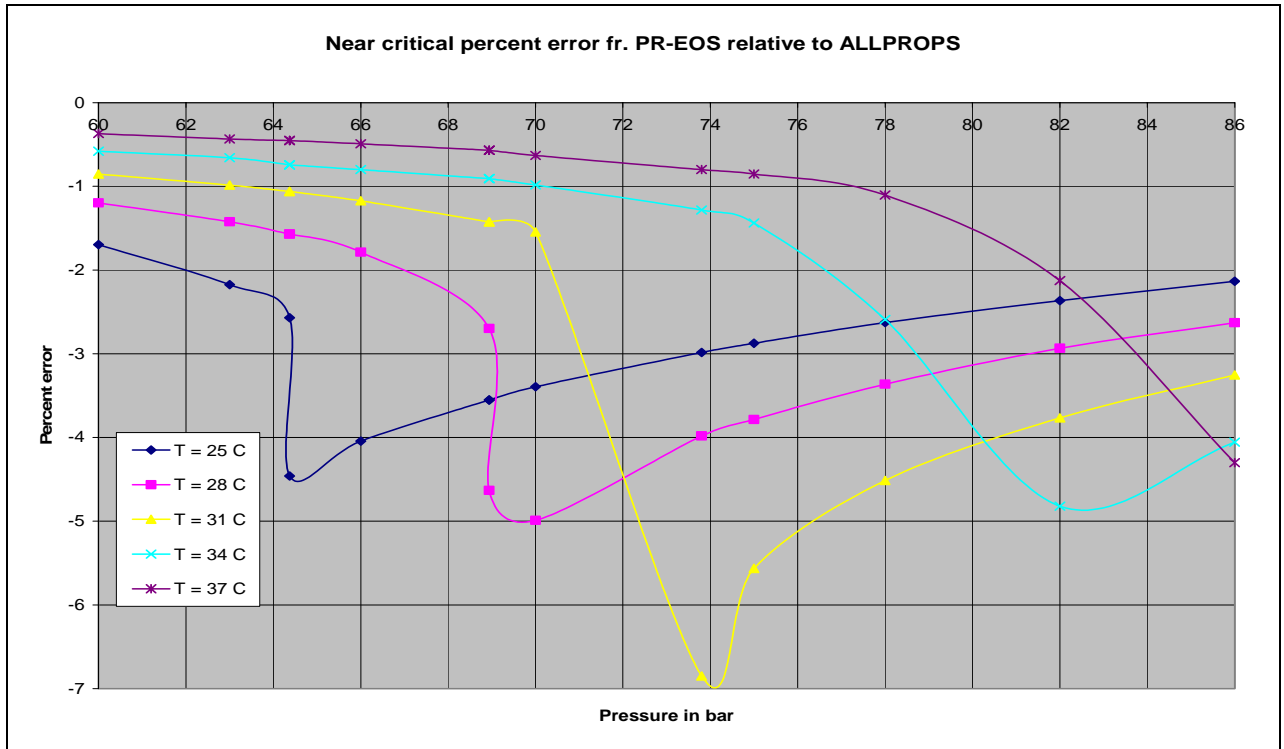


Fig. 3.2.6.10 CO₂ Entropy percent error near critical area from PR-EOS

Some points from entropy graphs above:

- The temperature increase at constant pressure always causes the increase of entropy and the increase of pressure at constant temperature causes the entropy to decrease, except at very low temperature and near saturated liquid area. The change of entropy is rapid at low pressure for gas phase and get slower as the pressure continue to increase. For liquid phase, the change of entropy due to pressure increase can be assumed linier.
- The same trends are shown in every graph for every equation of state used in this work. At low temperature, the value of entropy which estimated by EOS's varies larger at high pressure. But when the temperature is high, the variation of entropy value getting smaller.
- Saturated liquid is more uncertain compared with saturated gas as seen in the saturated entropy graph.
- Below is the table of entropy percent error in area of interest and near critical area:

Method	Entropy percent error		Entropy percent error	
	Area of interest		Near critical area	
	Min.	Max.	Min.	Max.
Peng-Robinson	-4	3	-7	0
Starling-BWR	-5	15	-21	5
Soave-Redlich-Kwong	-3	3	-7	0
ALLPROPS				

Table 3.2.6.1 CO₂ Entropy percent error

- It is different with enthalpy and internal energy which have large percent error, entropy has much smaller percent error. The explanation for this may be due to direct derivation of entropy departure function from EOS without involving other parameters (e.g. specific volume) which surely contain error. So, we can assume no error accumulation when calculating the departure function of entropy.

3.2.7.1 CO₂ Constant Pressure Specific Heat- Pressure plot

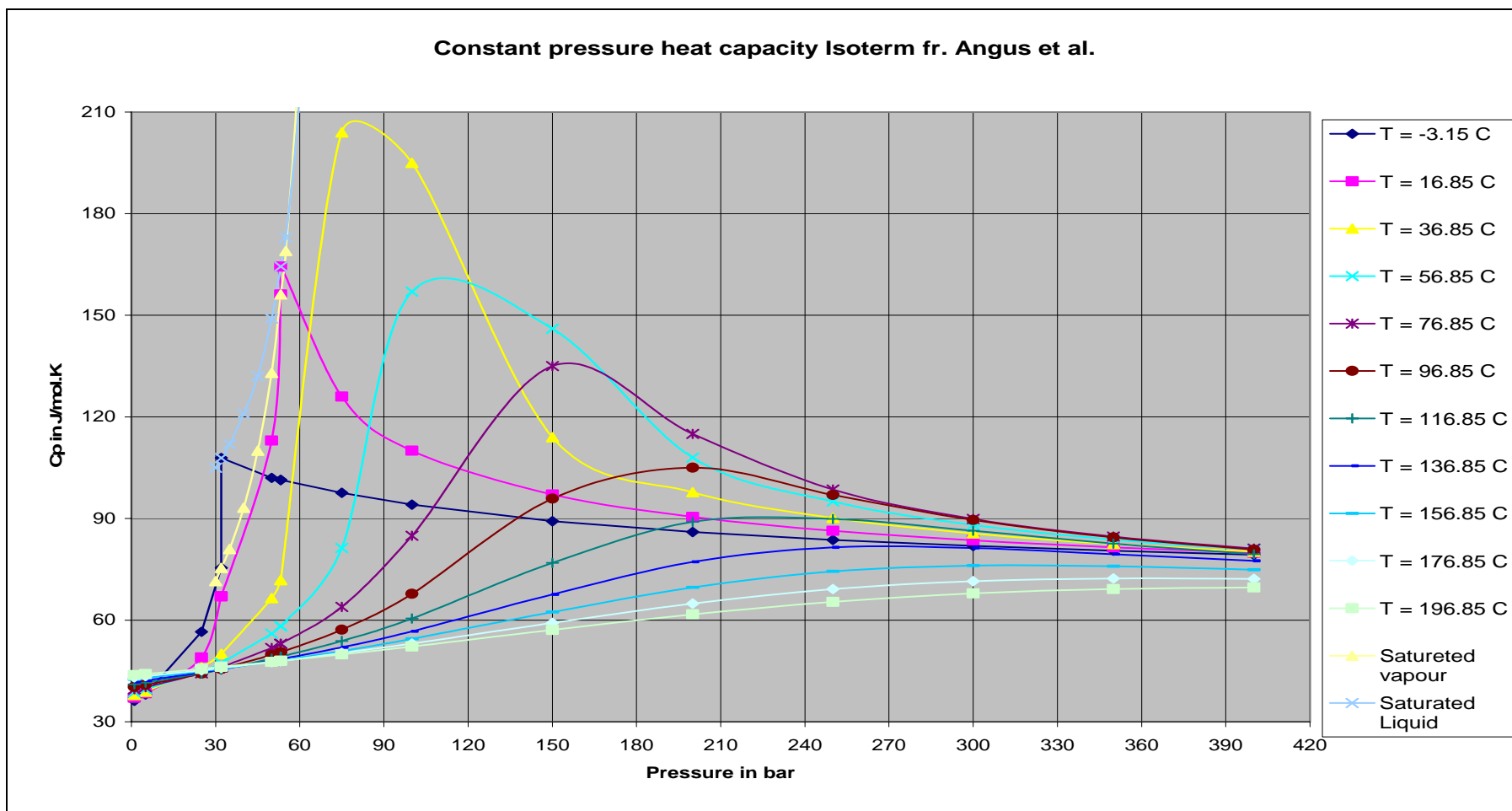


Fig.3.2.7.1 CO₂ Constant Pressure Specific Heat-Pressure plot for many isotherms (taken from Angus et al.)

3.2.7.2 Comparison of CO₂ Constant Pressure Specific Heat

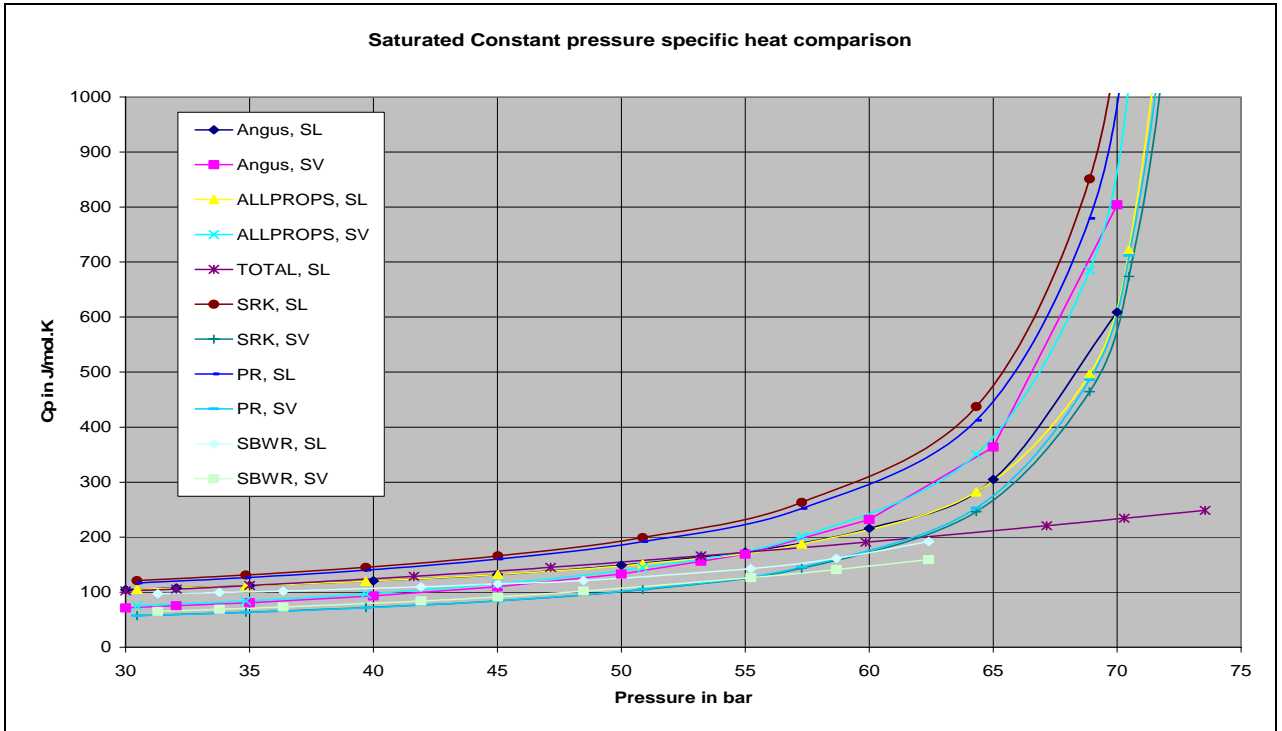


Fig. 3.2.7.2 Saturated CO₂ Constant Pressure Specific Heat comparison

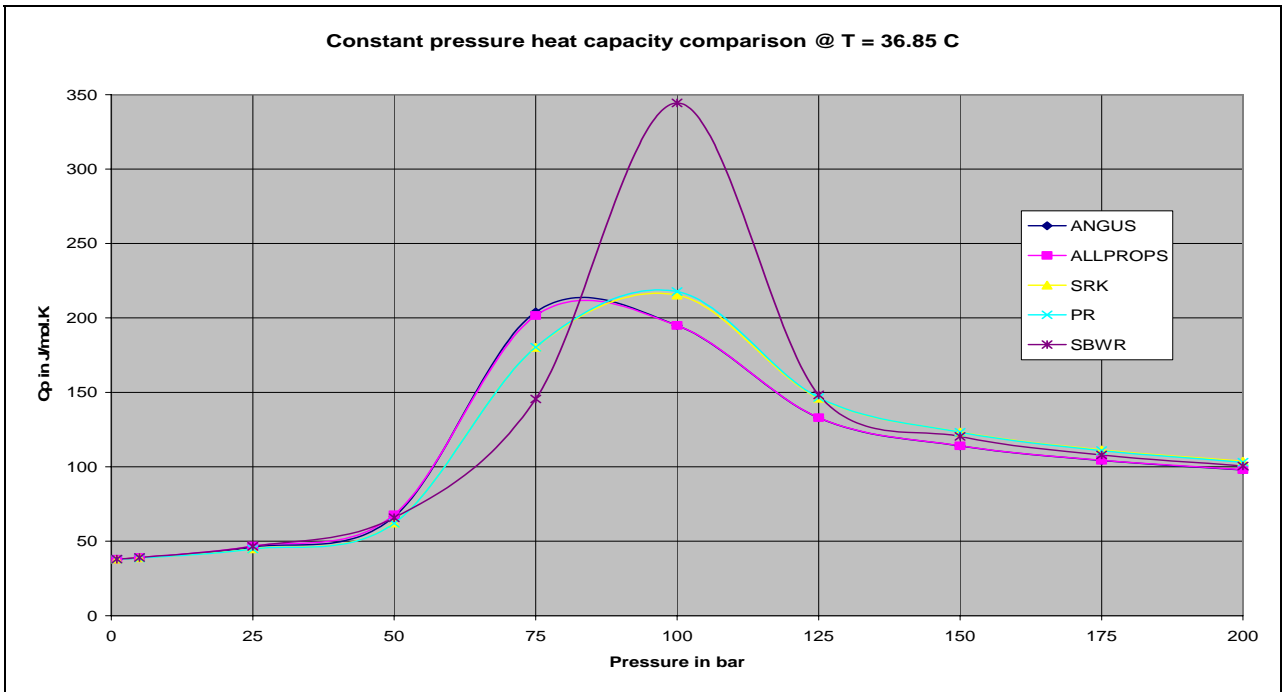


Fig 3.2.7.3 CO₂ Constant Pressure Specific Heat comparison at T = 36.85 °C

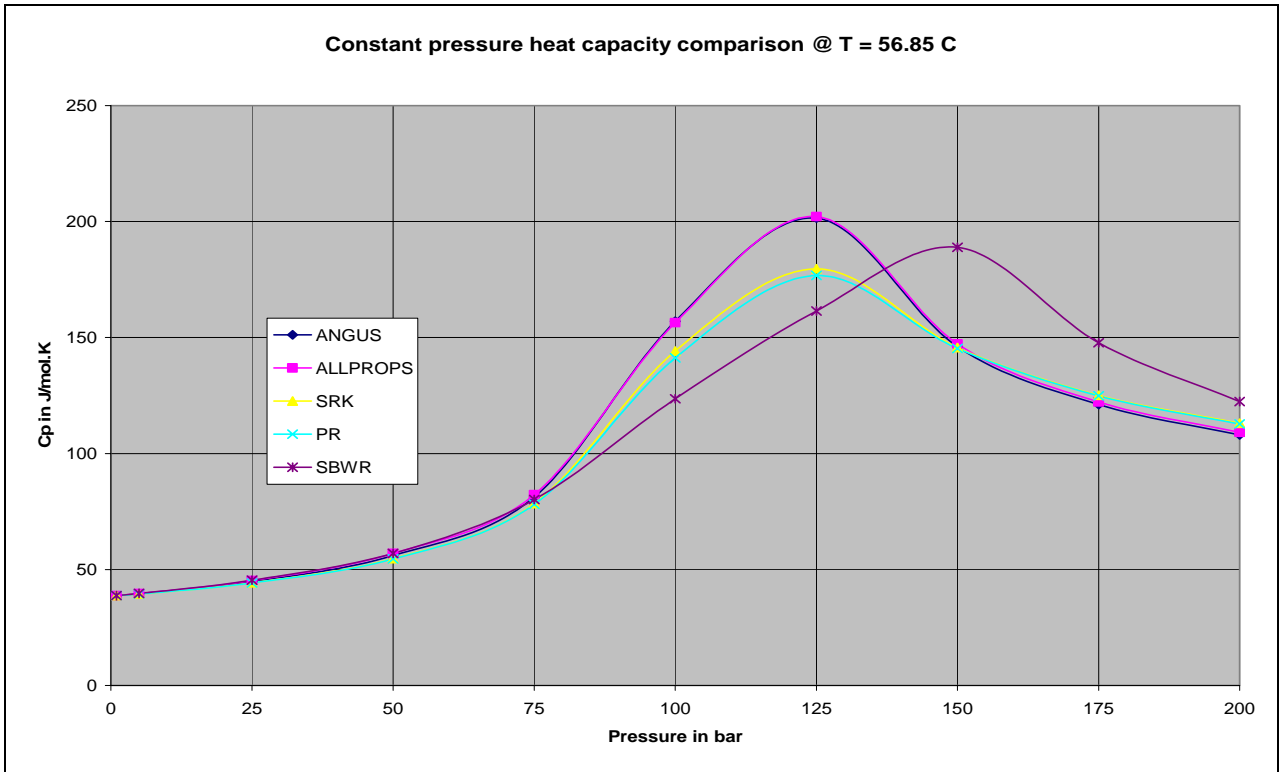


Fig 3.2.7.4 CO₂ Constant Pressure Specific Heat comparison at T = 56.85 °C

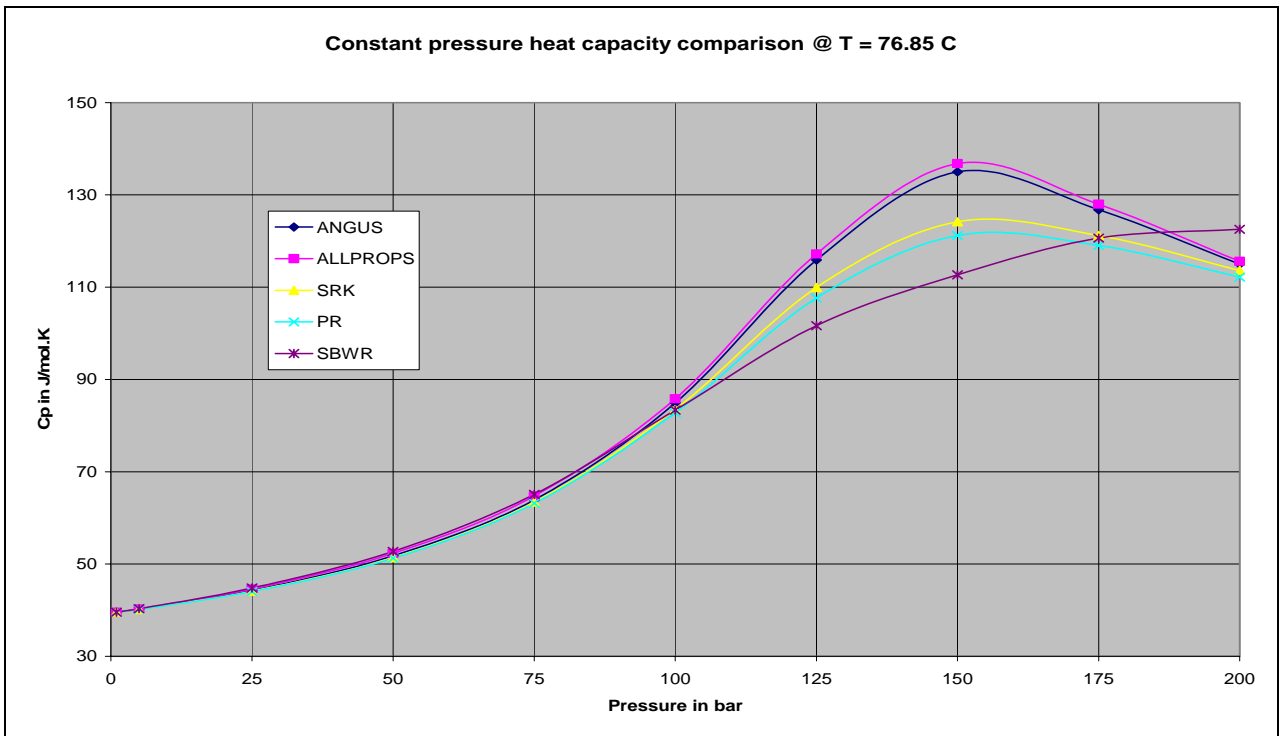


Fig 3.2.7.5 CO₂ Constant Pressure Specific Heat comparison at T = 76.85 °C

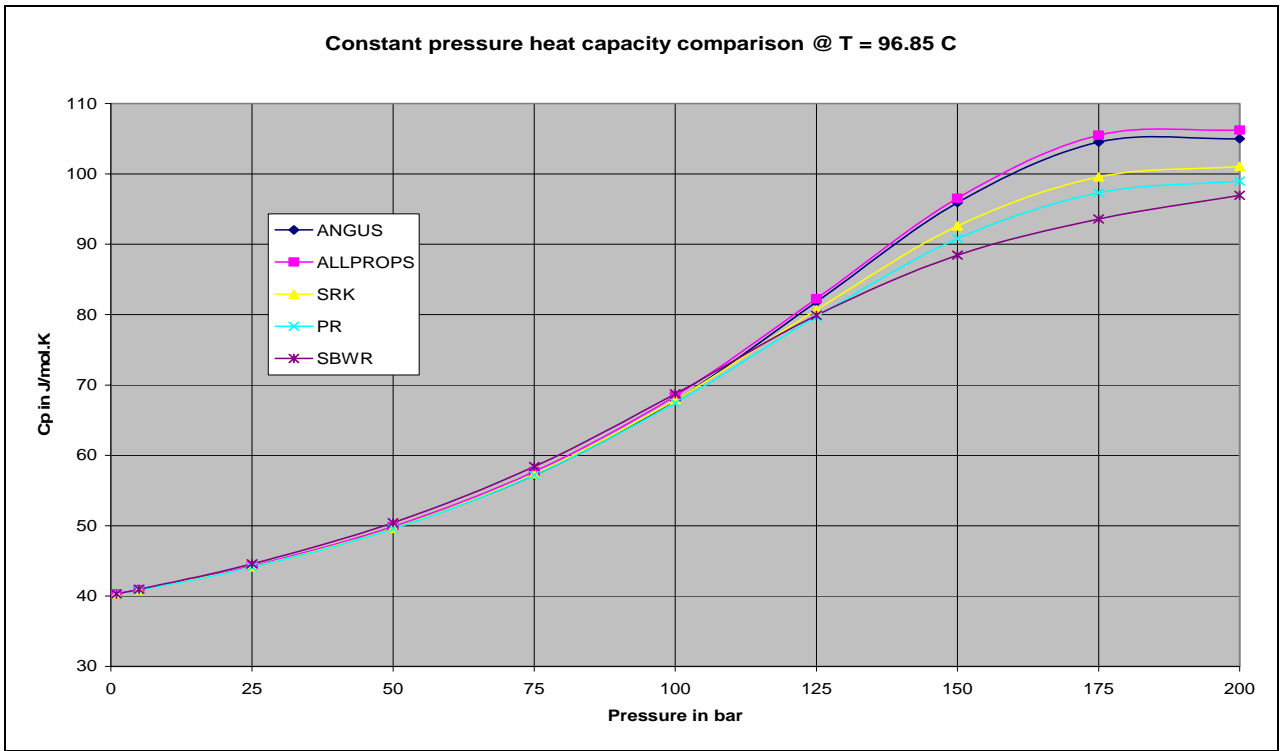


Fig 3.2.7.6 CO₂ Constant Pressure Specific Heat comparison at T = 96.85 °C

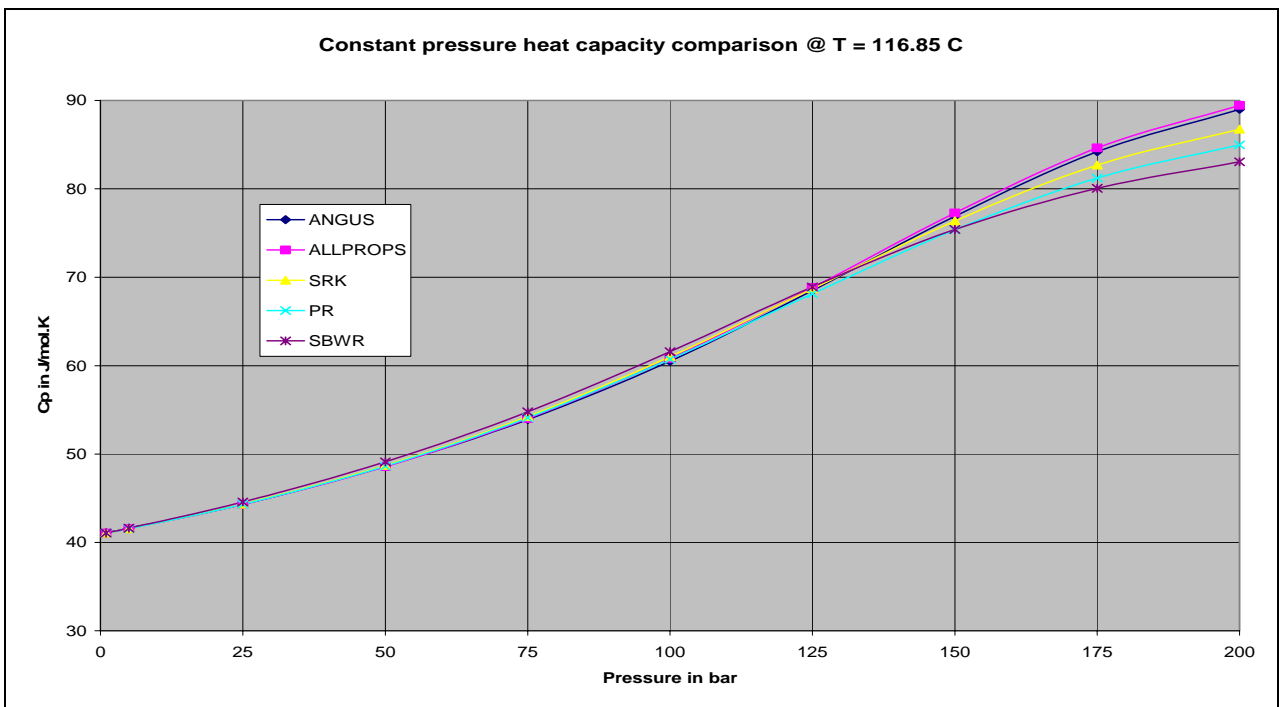


Fig 3.2.7.7 CO₂ Constant Pressure Specific Heat comparison at T = 116.85 °C

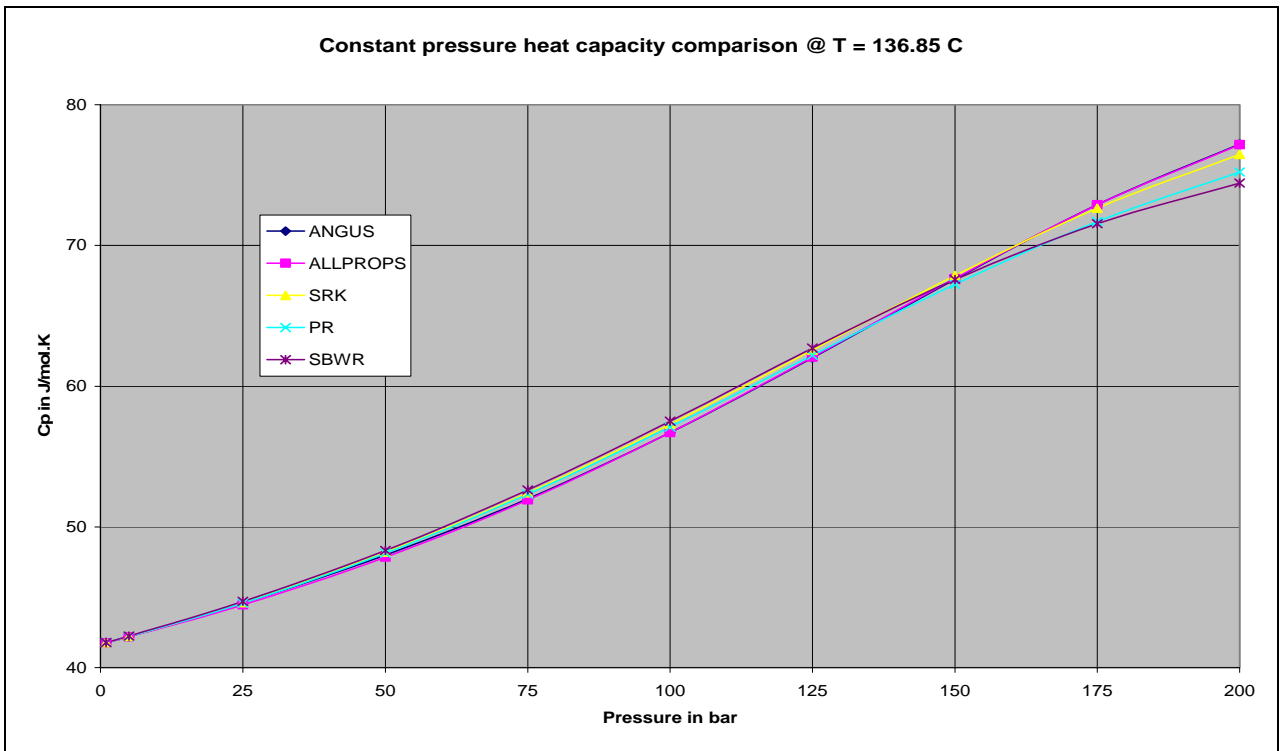


Fig 3.2.7.8 CO₂ Constant Pressure Specific Heat comparison at T = 136.85 °C

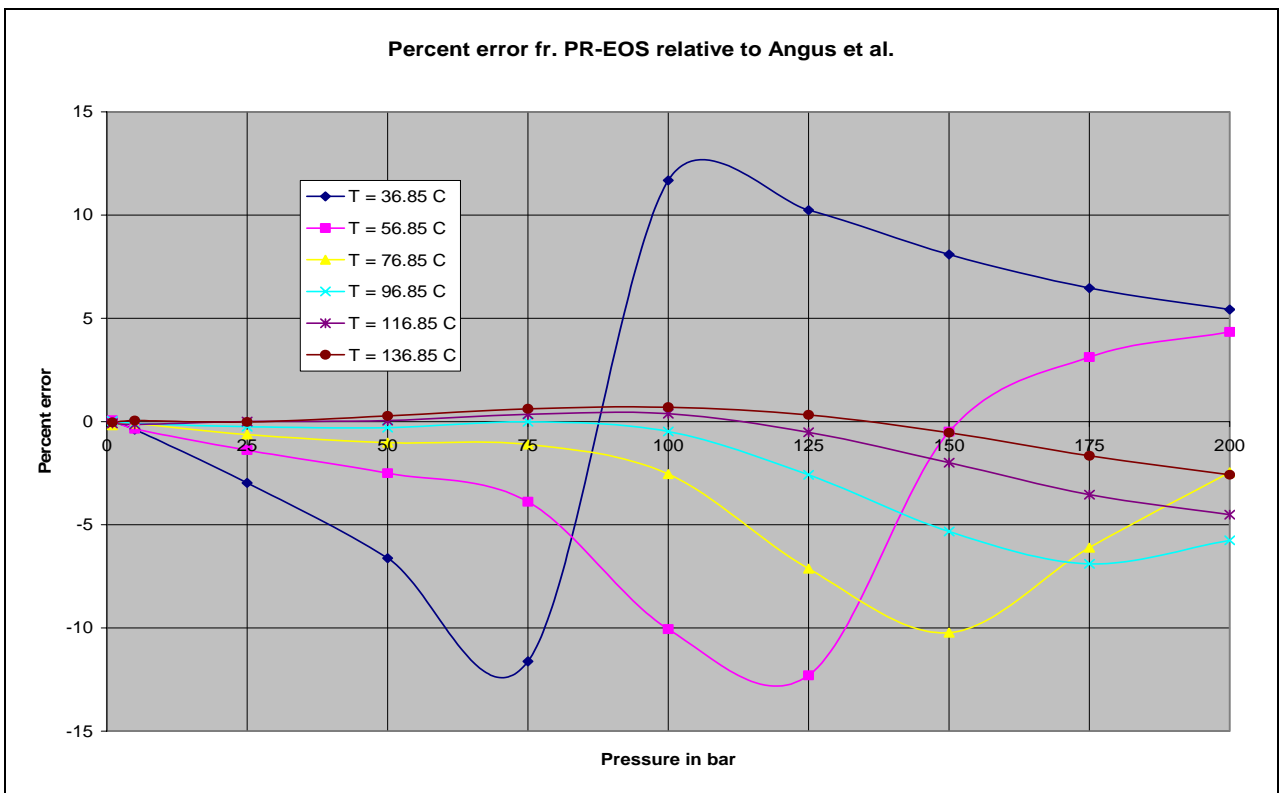


Fig 3.2.7.9 CO₂ Constant Pressure Specific Heat percent error at area of interest, PR-EOS

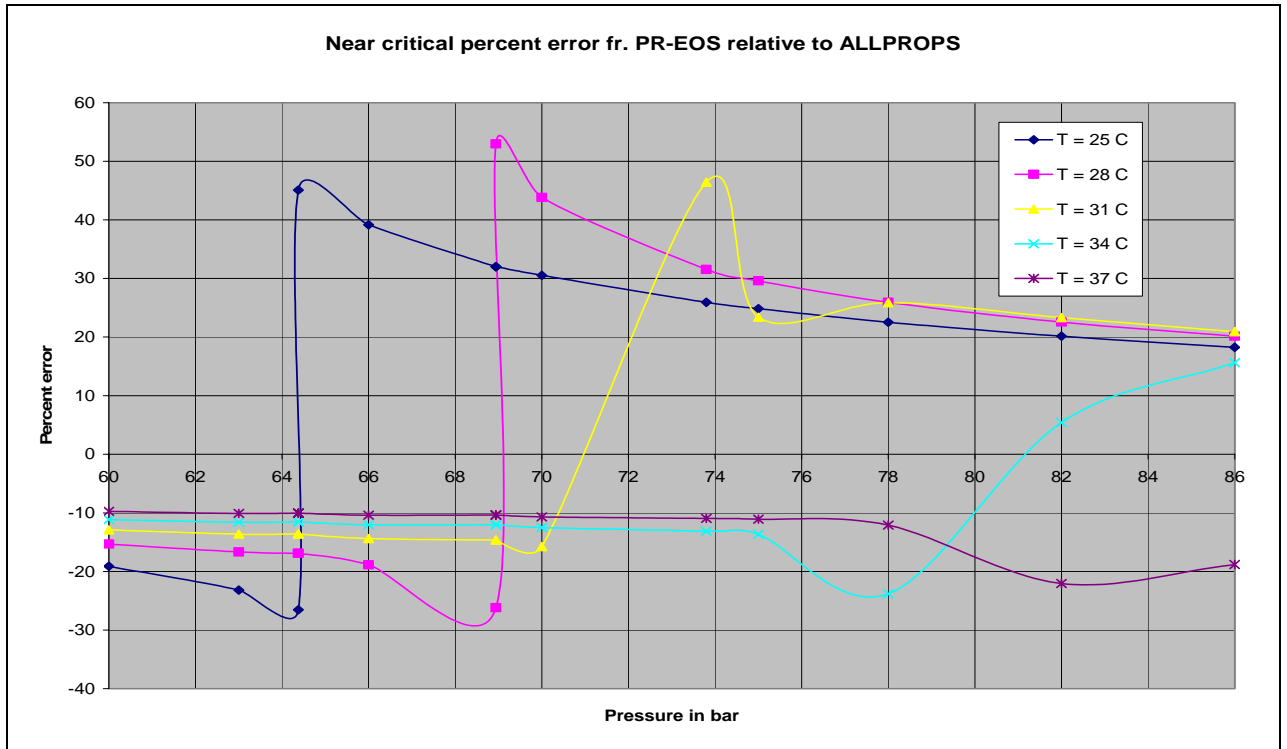


Fig 3.2.7.10 CO₂ Constant Pressure Specific Heat percent error near critical area from PR-EOS

Some points from the Constant Pressure Specific Heat graphs above:

- At low temperature, constant pressure specific heat forms “bell shape” when the pressure is increased at the constant temperature (i.e. isotherm) while at high temperature, the increase of pressure at constant temperature causes the increase of constant pressure specific heat, but not linearly.
- At critical point, the value of constant pressure specific heat is very high. Thus saturated liquid and gas line abruptly rise significantly (similar to shock wave) then meet at critical value of constant pressure specific heat. It is difficult to distinguish between liquid and gas constant pressure specific heat toward closer to critical point. The value itself has the high uncertainty due to uncertainty in how the constant pressure specific heat changes with the changes of pressure and temperature near to critical point.
- There is cross point between saturated liquid line and saturated gas line. At low pressure, saturated liquid has higher value of constant pressure specific heat than

saturated gas but when the pressure increases until a certain pressure (before critical pressure), the “position” changed, saturated liquid becomes lower than saturated gas.

- TOTAL recommendation to estimate the saturated liquid seems have good accuracy for the pressure less than 60 bar (i.e. saturated temperature ca. 22 °C), but after that, the trend is linear which couldn't describe the behavior near to critical point.
- Generally, the same pattern is met but the variation exists. At low temperature, great variation of constant pressure specific heat that predicted by EOS's occurs at near the peak of bell shape and for high temperature, it occurs at high pressure.
- Below is the table of constant pressure specific heat percent error in area of interest and near critical area:

Method	Cp percent error		Cp percent error	
	Area of interest		Near critical area	
	Min.	Max.	Min.	Max.
Peng-Robinson	-15	15	-30	55
Starling-BWR	-40	80	-100	140
Soave-Redlich-Kwong	-15	15	-40	70
ALLPROPS	-1.5	2.5		

Table 3.2.7.1 CO₂ Constant Pressure Specific Heat percent error

The reference for area of interest is Angus et al. [1] while for near critical area is ALLPROPS. SBWR-EOS gives the largest uncertainty in area of interest when being used to estimate constant pressure specific heat even though it estimates density value very well.

3.2.8.1 CO₂ Constant Volume Specific Heat-Pressure plot

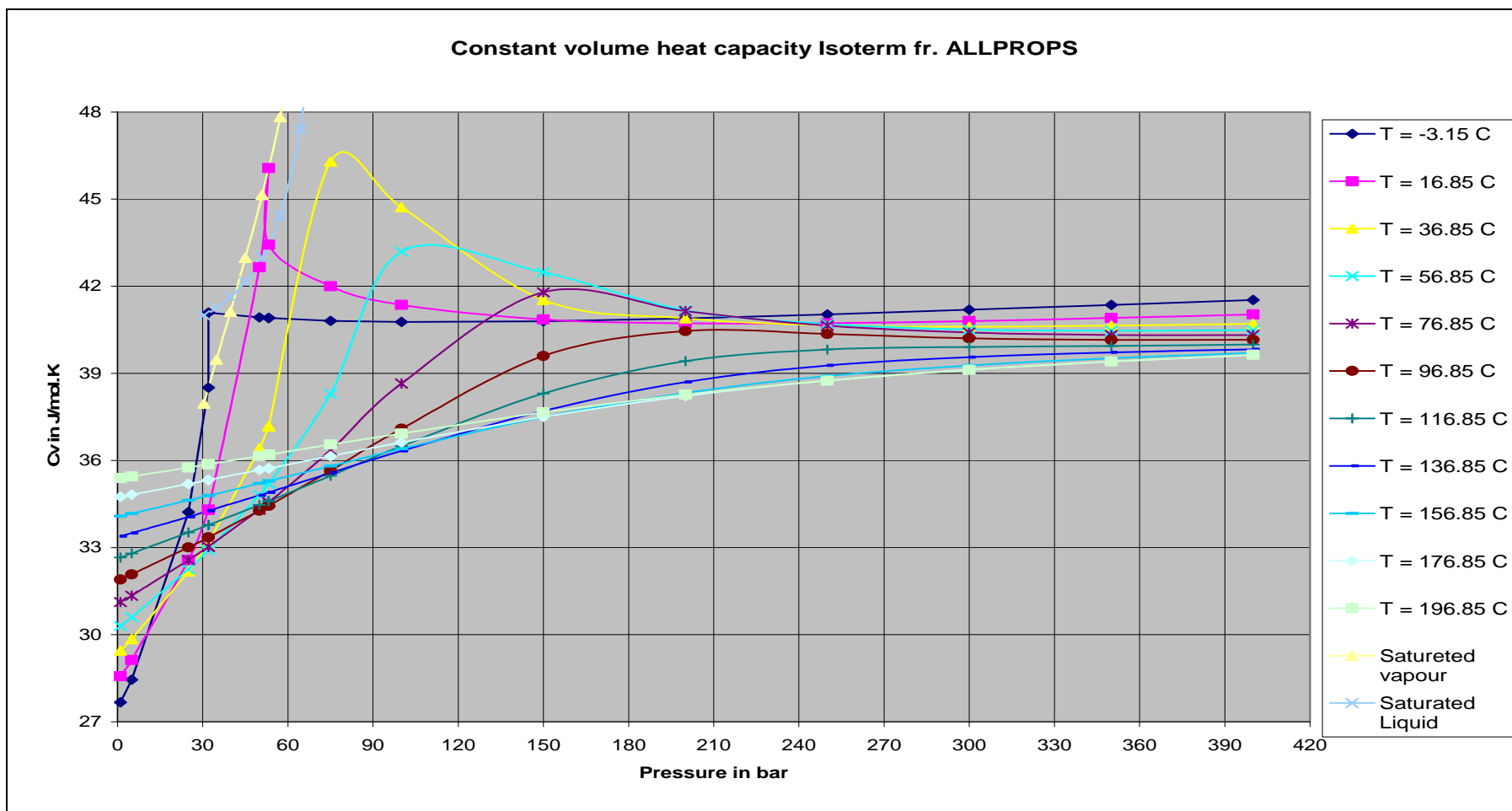


Fig. 3.2.8.1 CO₂ Constant Volume Specific Heat-Pressure plot for many isotherms (*obtained from ALLPROPS*)

3.2.8.2 Comparison of CO₂ Constant Volume Specific Heat

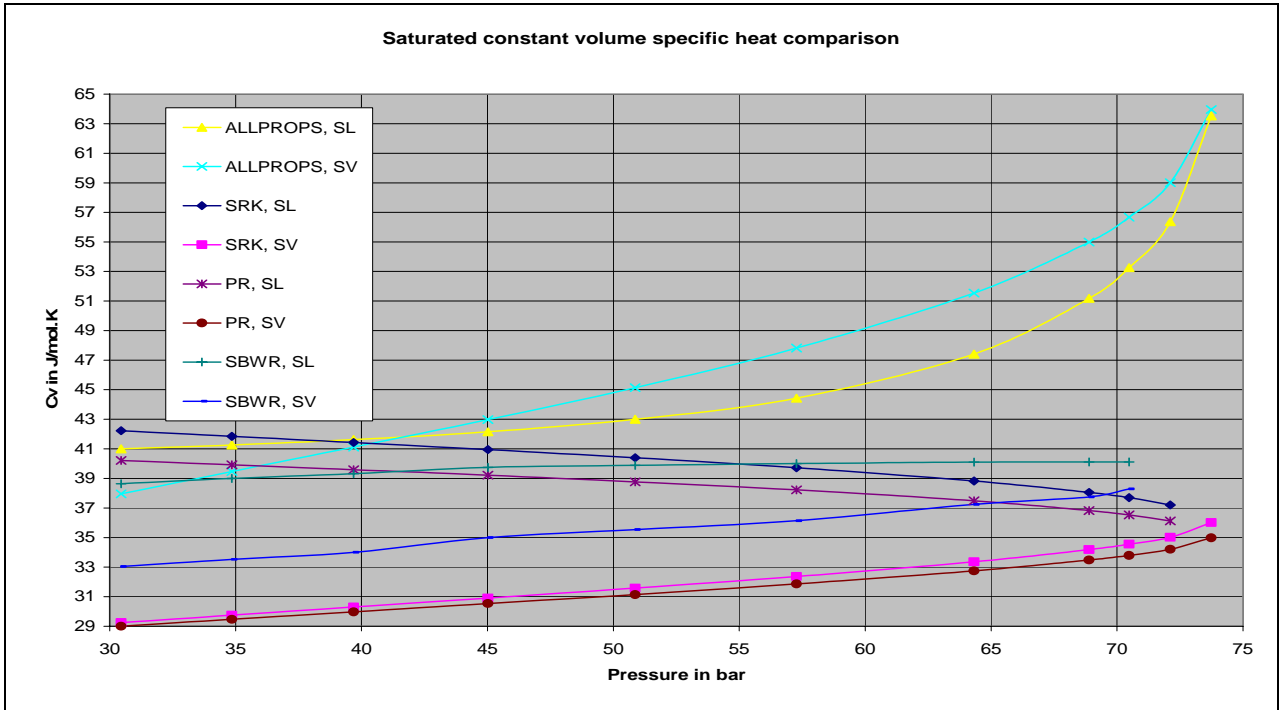


Fig. 3.2.8.2 Saturated CO₂ Constant Volume Specific Heat comparison

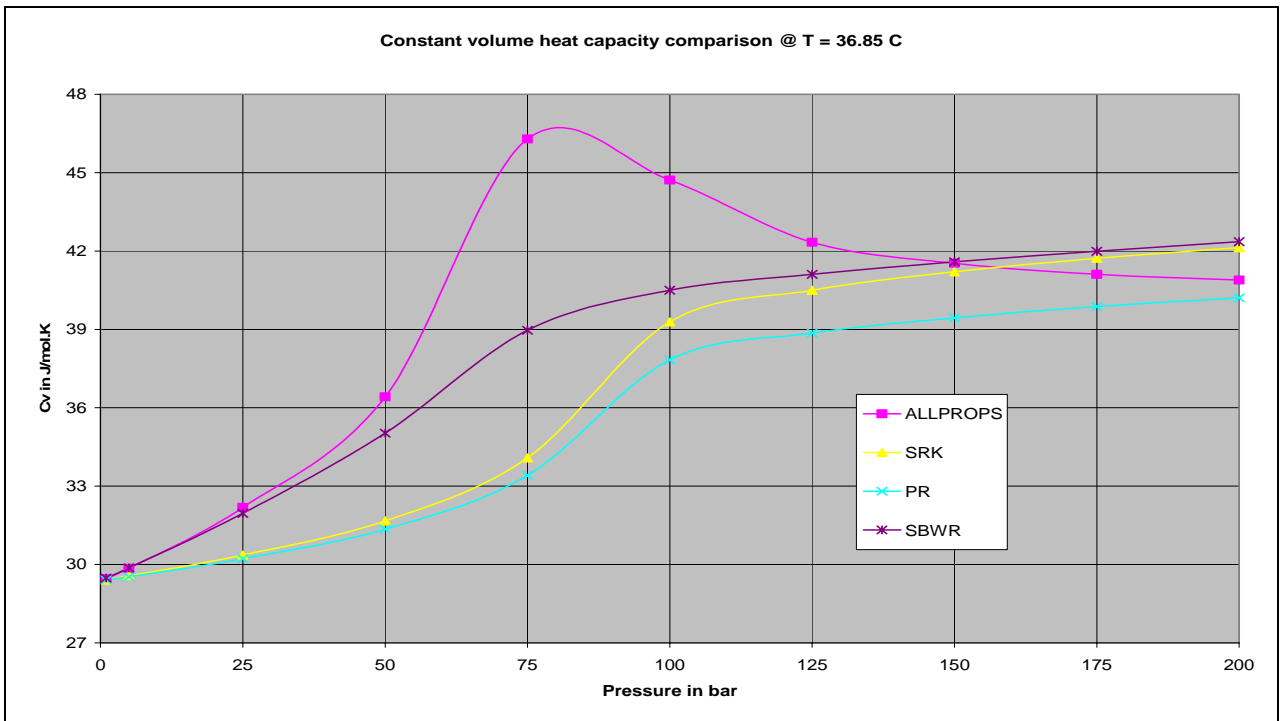


Fig 3.2.8.3 CO₂ Constant Volume Specific Heat comparison at T = 36.85 °C

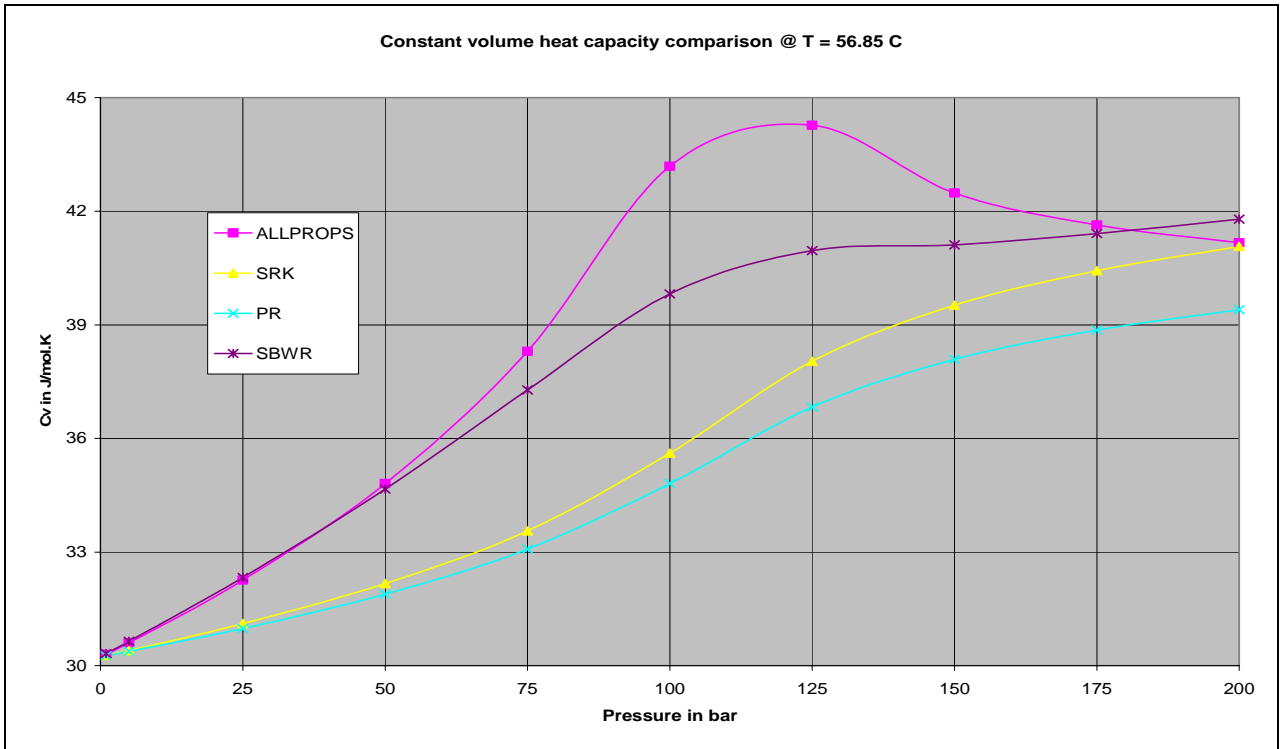


Fig 3.2.8.4 CO₂ Constant Volume Specific Heat comparison at T = 56.85 °C

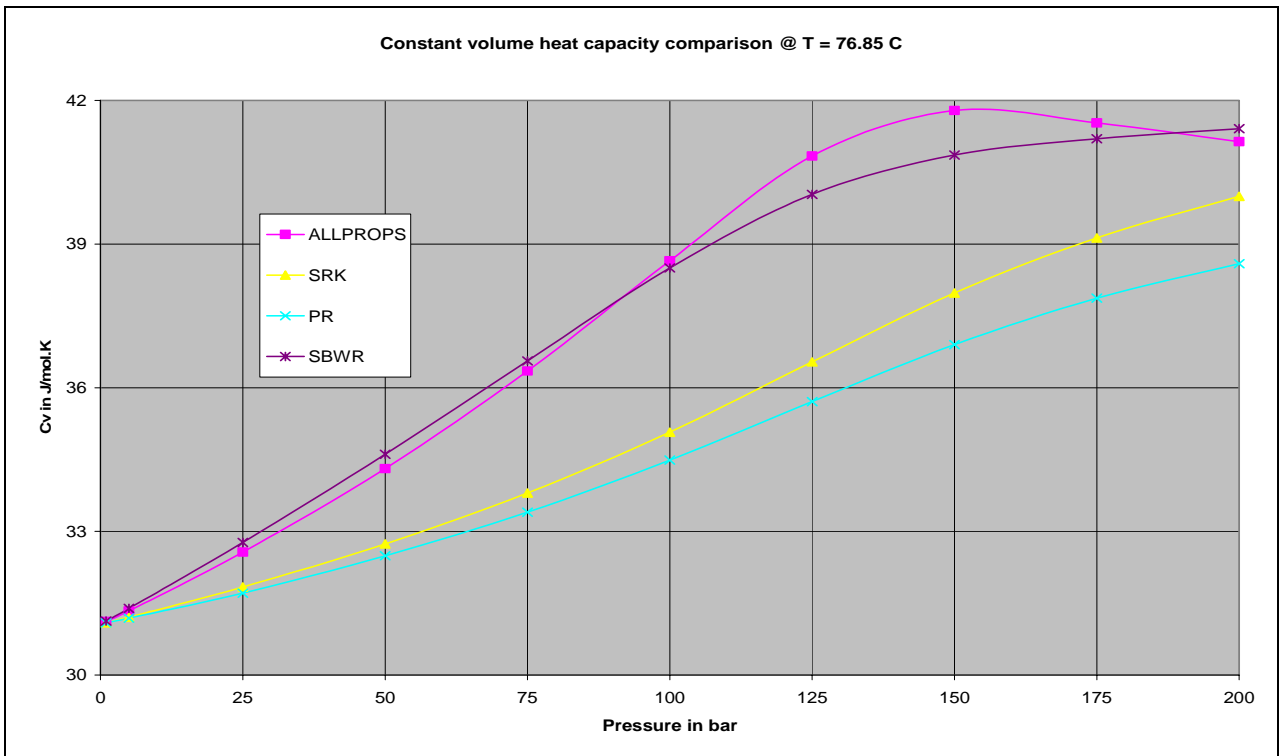


Fig 3.2.8.5 CO₂ Constant Volume Specific Heat comparison at T = 76.85 °C

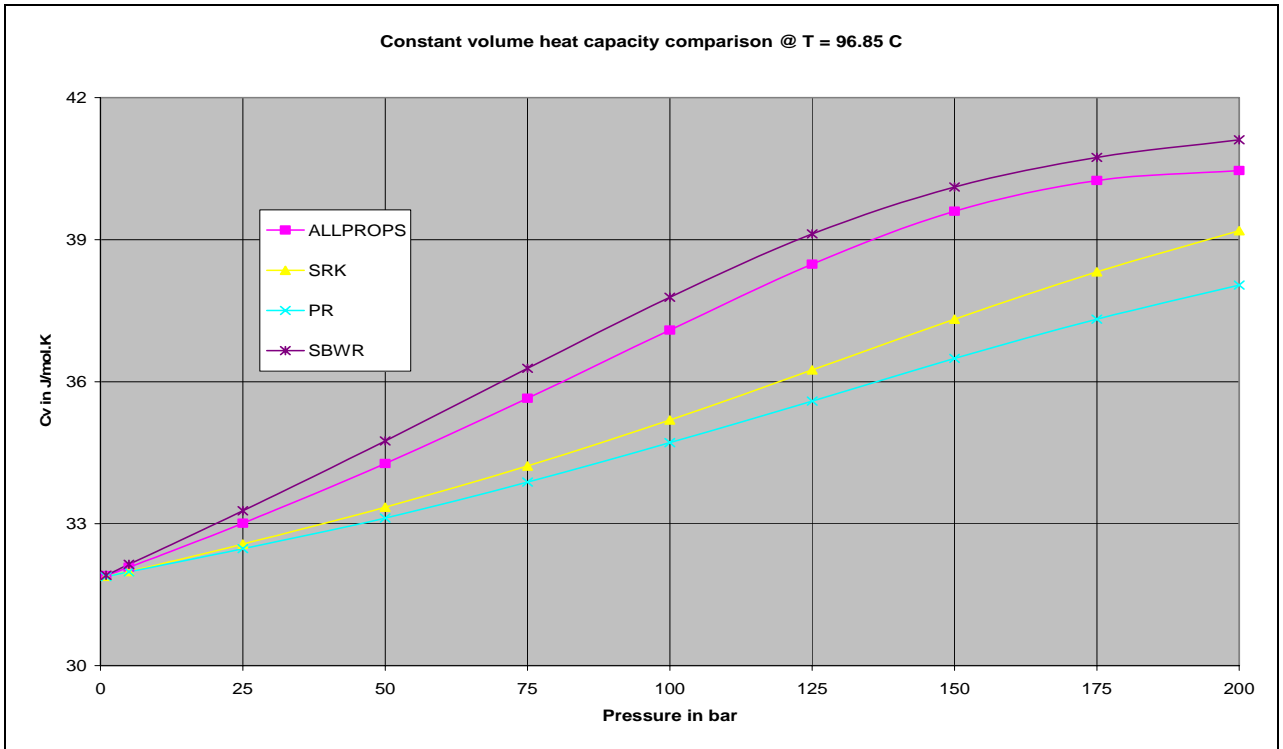


Fig 3.2.8.6 CO₂ Constant Volume Specific Heat comparison at T = 96.85 °C

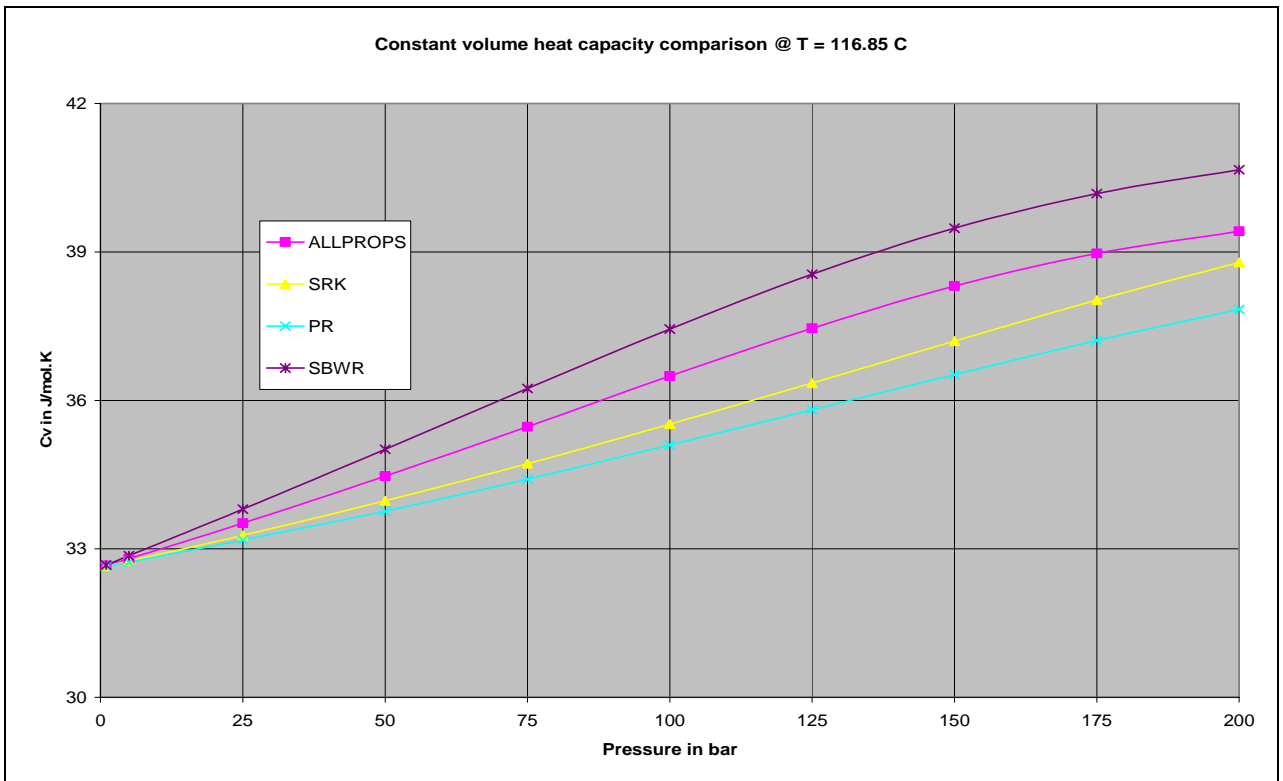


Fig 3.2.8.7 CO₂ Constant Volume Specific Heat comparison at T = 116.85 °C

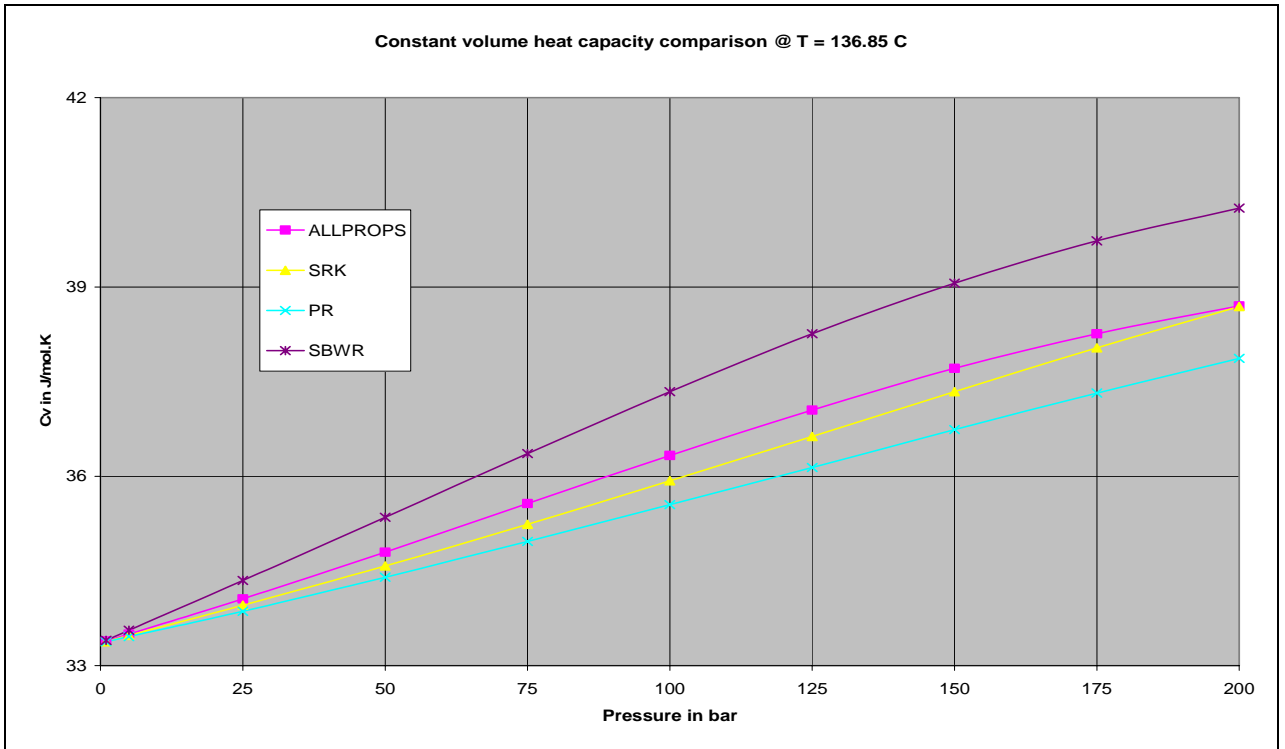


Fig 3.2.8.8 CO₂ Constant Volume Specific Heat comparison at T = 136.85 °C

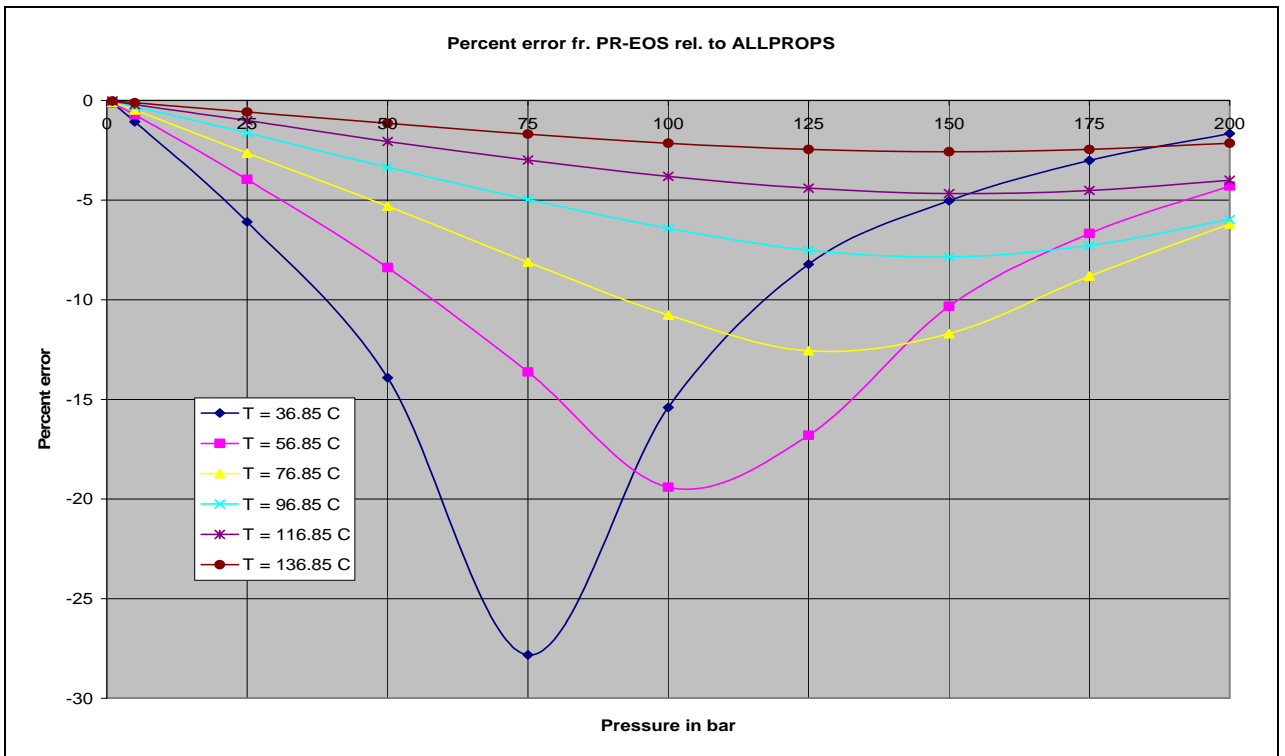


Fig 3.2.8.9 CO₂ Constant Volume Specific Heat percent error at area of interest, PR-EOS

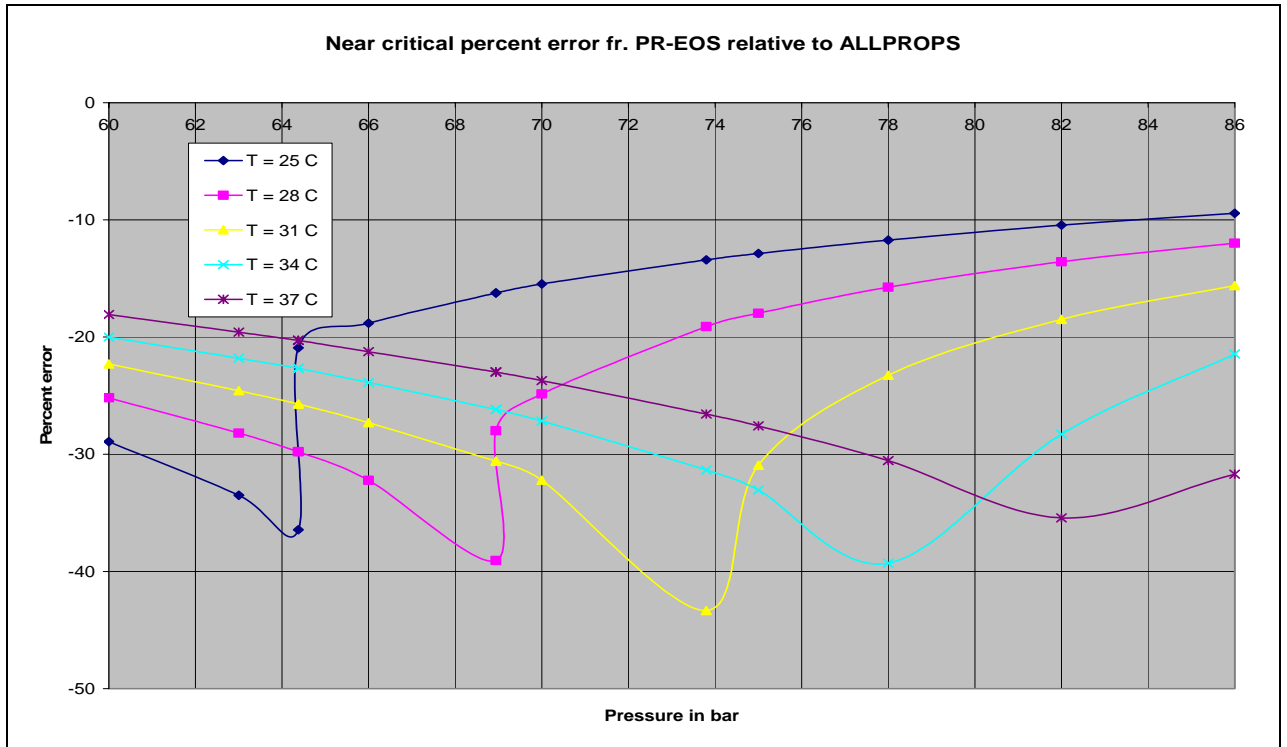


Fig 3.2.8.10 CO₂ Constant Volume Specific Heat percent error near critical area from PR-EOS

Some points from constant volume specific heat graphs above:

- All the graphs similar to constant pressure specific heat graphs. The only difference is the value. Constant volume specific heat always has lower value than constant pressure specific heat. Thus, the explanation of graphs is the same with the constant pressure specific heat.
- At the critical point, all cubic EOS that we used tends to construct the “normal envelope” rather than the envelope formed by ALLPROPS. It means at critical point, EOS’s predict much smaller value of constant volume specific heat rather than the abrupt high value like ALLPROPS does. Another thing is there is no cross point anywhere in saturation zone for EOS’s prediction which is contrary with ALLPROPS.
- Below is the table of constant volume specific heat at area of interest and near critical region:

Method	Cv percent error		Cv percent error	
	Area of interest		Near critical area	
	Min.	Max.	Min.	Max.
Peng-Robinson	-28	0	-42	-9
Starling-BWR	-17	5	-36	-5
Soave-Redlich-Kwong	-27	5	-42	-5

Table 3.2.8.1 CO₂ Constant Volume specific heat percent error

From equations of state above, SBWR-EOS now gives the smallest uncertainty compared to others when being used to estimate the value of constant volume specific heat. This is opposite with its performance on constant pressure specific heat.

3.2.9.1 CO₂ Thermal Conductivity-Temperature plot

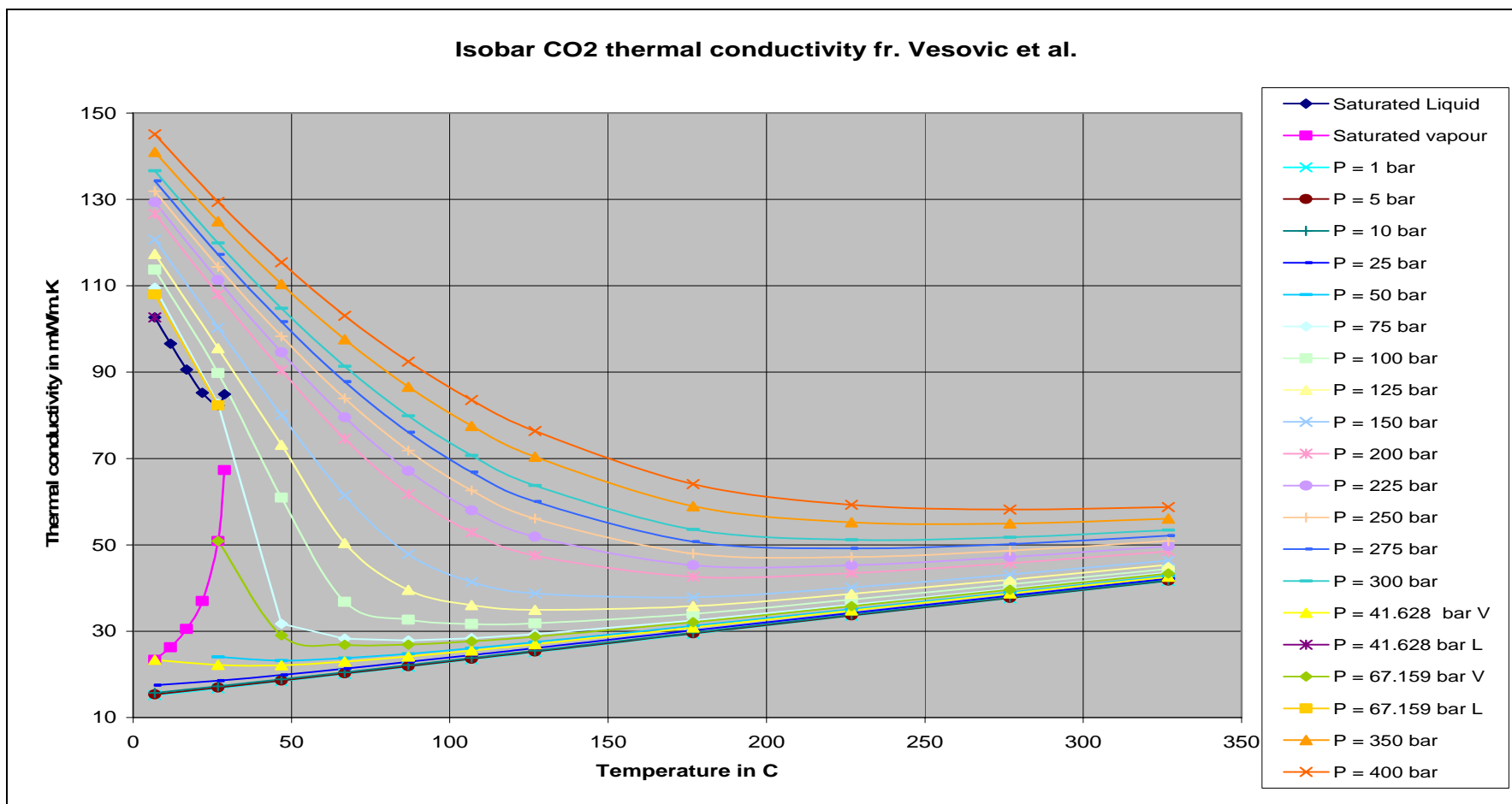


Fig.3.2.9.1 CO₂ Thermal Conductivity-Temperature plot for many isobars (taken from Vesovic et al.)

3.2.9.2 Comparison of CO₂ Thermal conductivity

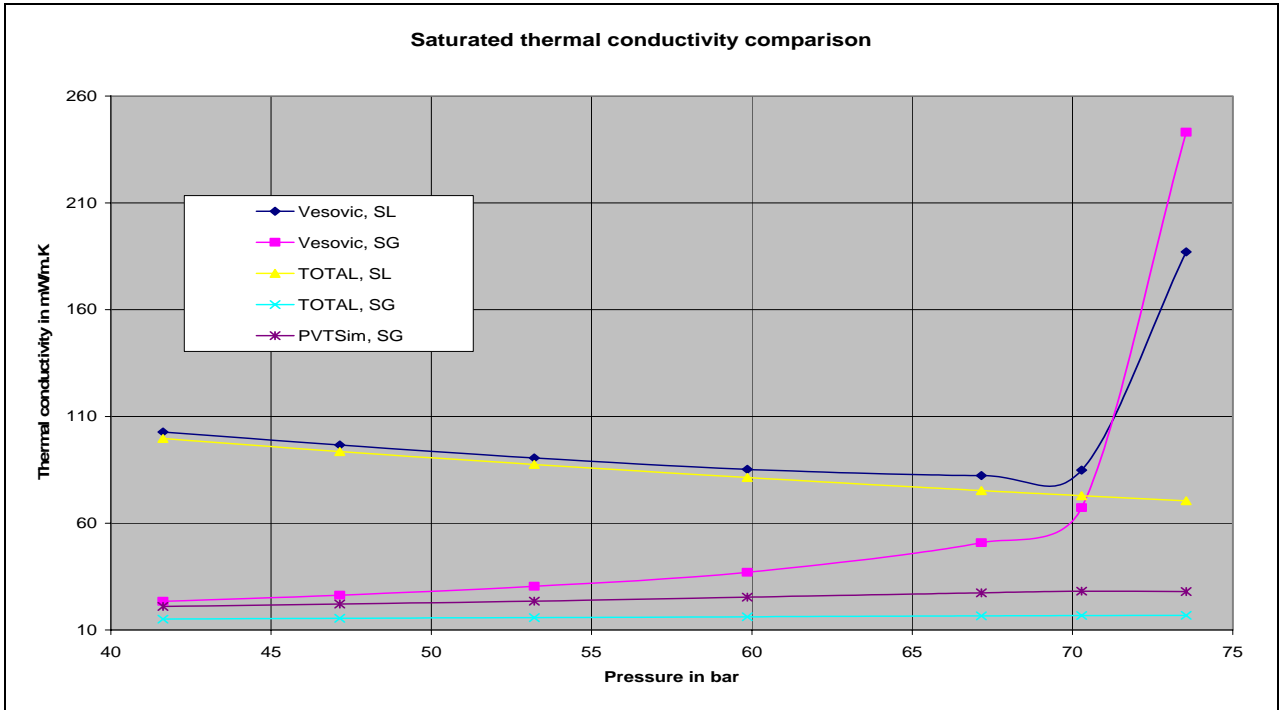


Fig. 3.2.9.2 Saturated CO₂ Thermal conductivity comparison

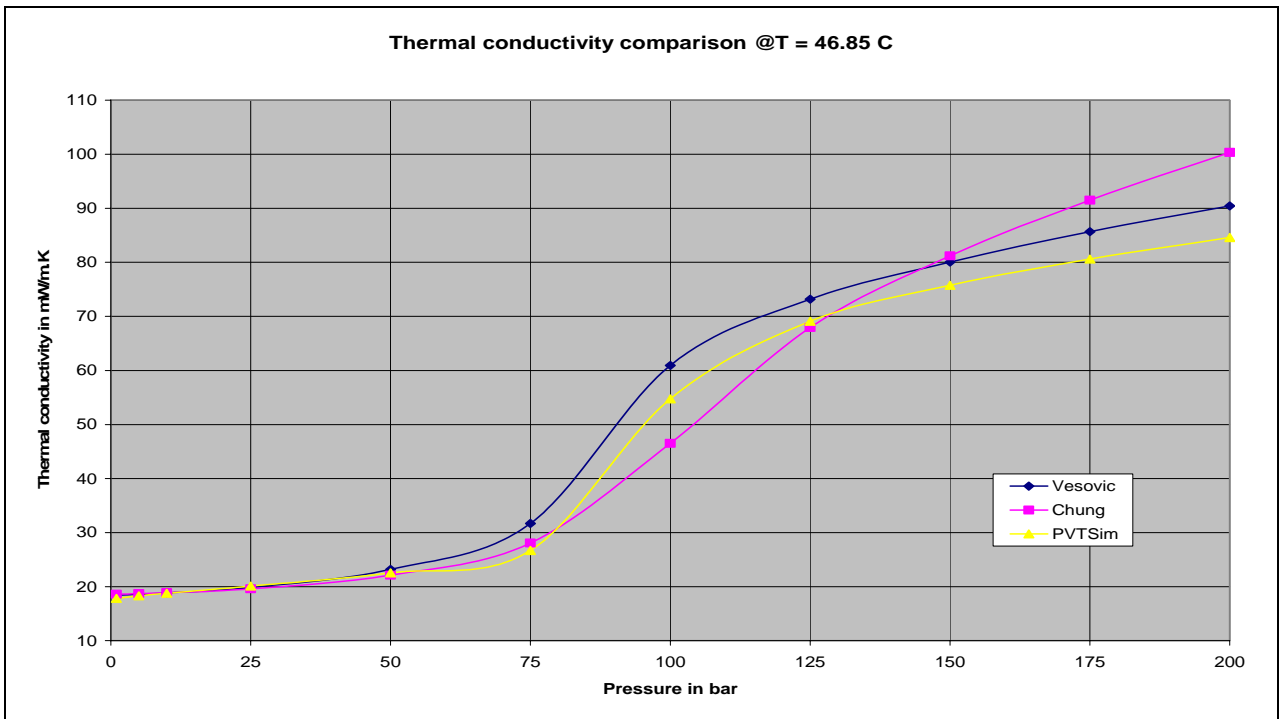


Fig 3.2.9.3 CO₂ Thermal conductivity comparison at T = 46.85 °C

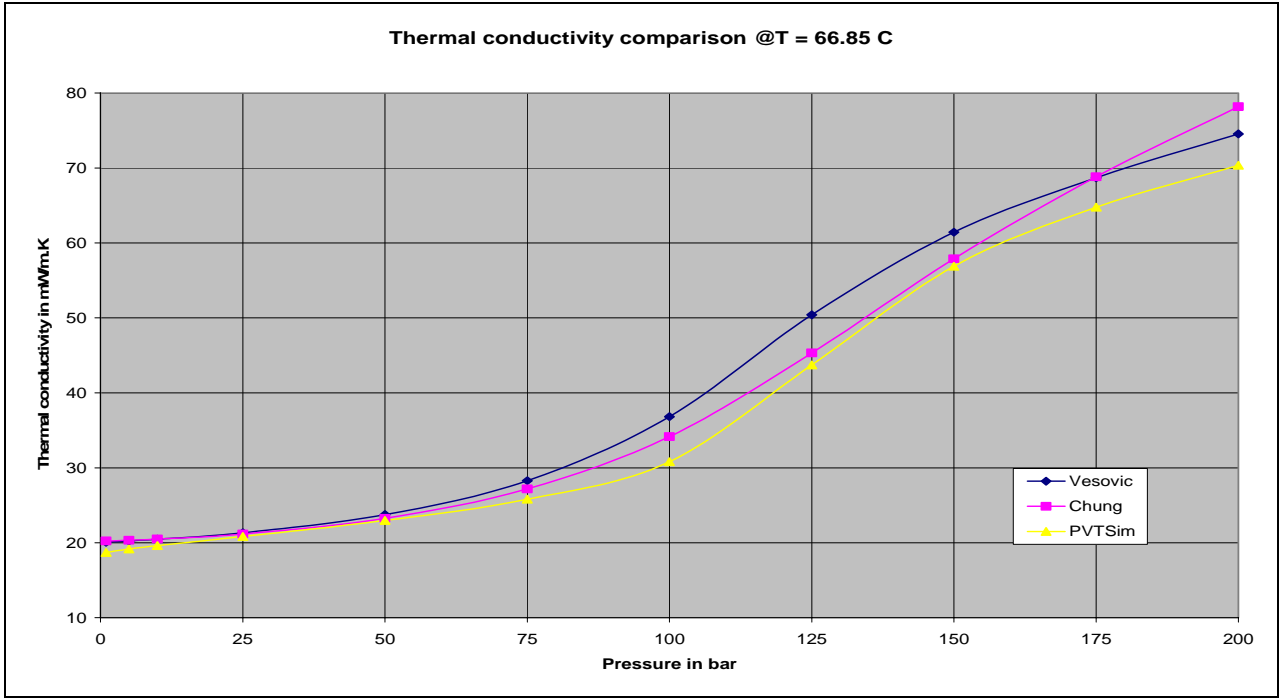


Fig 3.2.9.4 CO₂ Thermal conductivity comparison at T = 66.85 °C

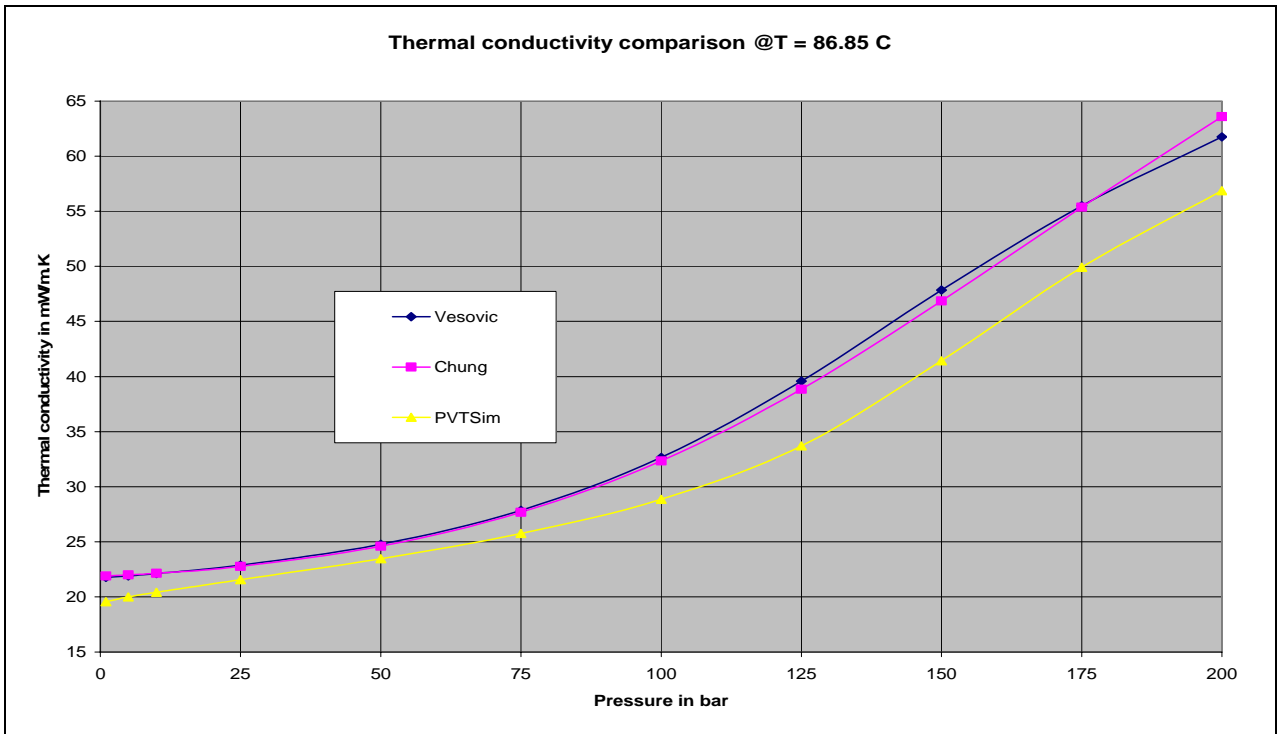


Fig 3.2.9.5 CO₂ Thermal conductivity comparison at T = 86.85 °C

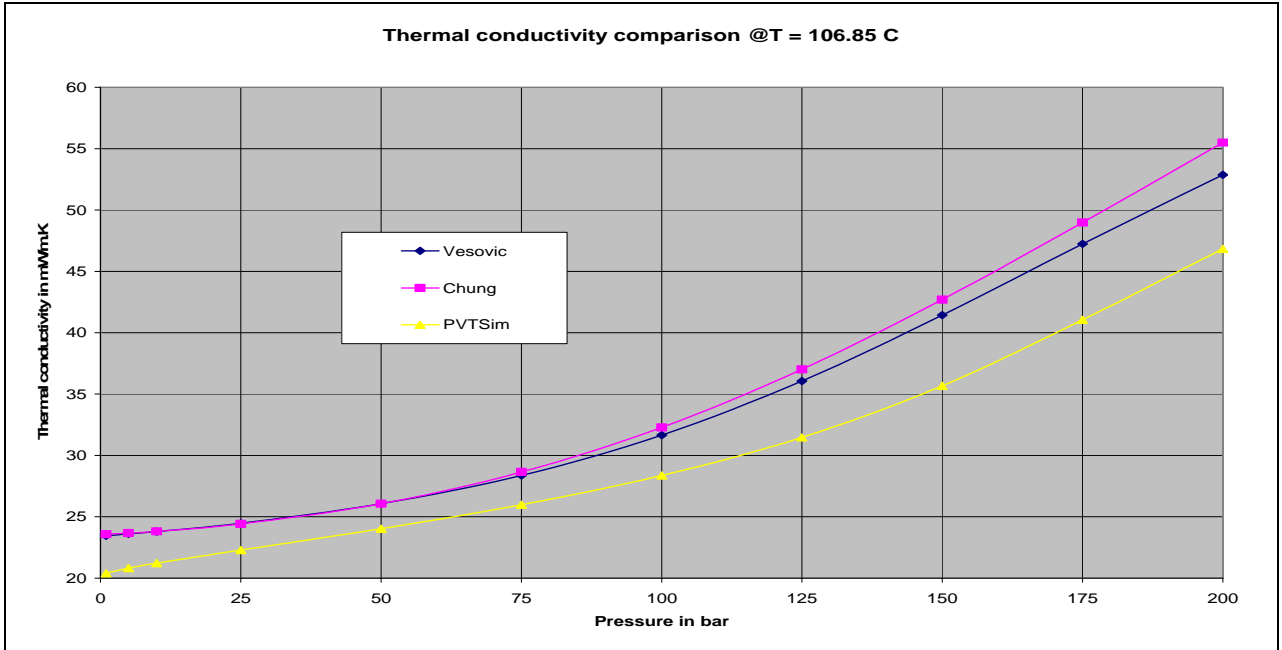


Fig 3.2.9.6 CO₂ Thermal conductivity comparison at T = 106.85 °C

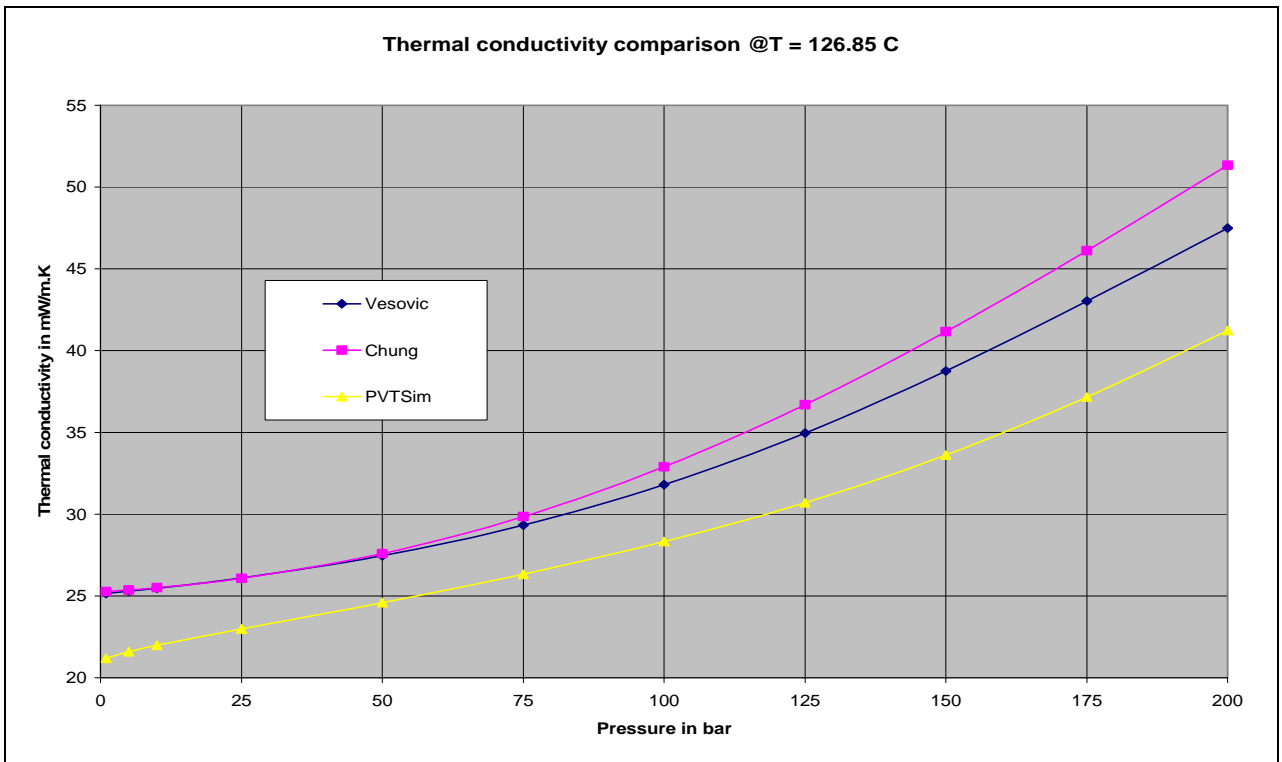


Fig 3.2.9.7 CO₂ Thermal conductivity comparison at T = 126.85 °C

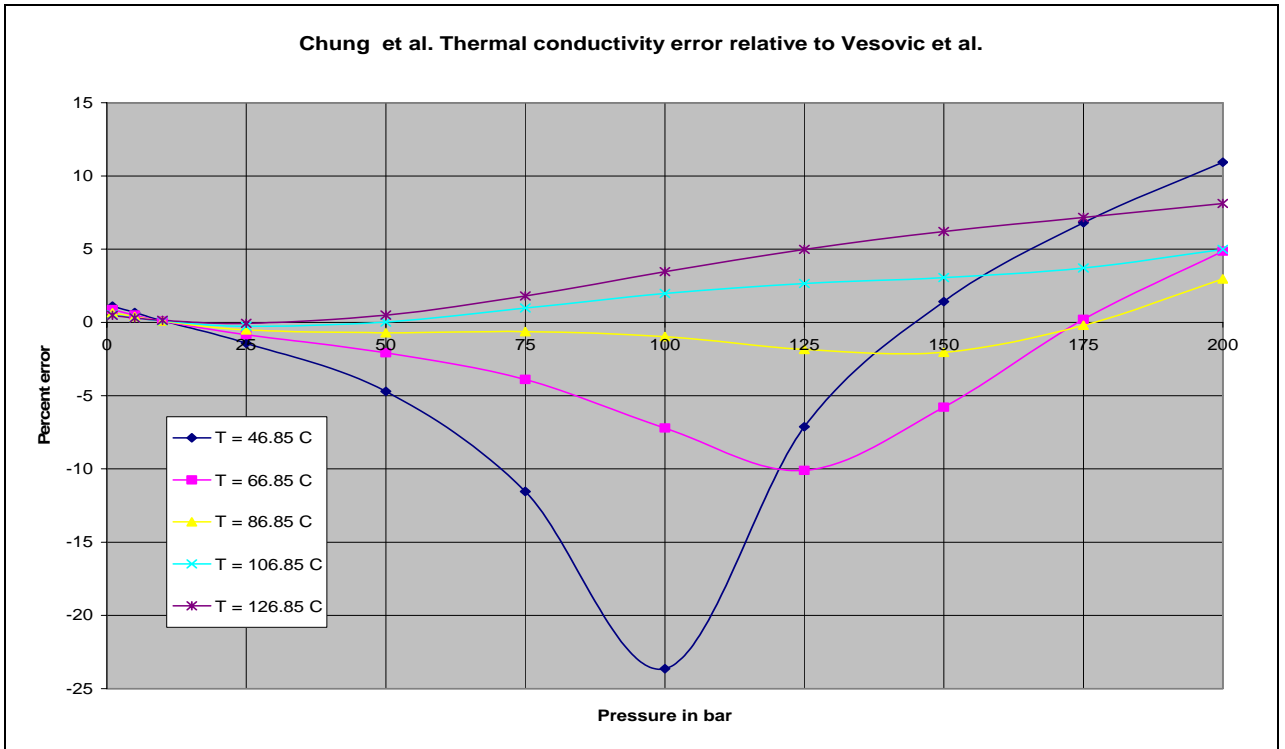


Fig. 3.2.9.8 CO₂ Thermal conductivity percent error at area of interest from Chung et al.

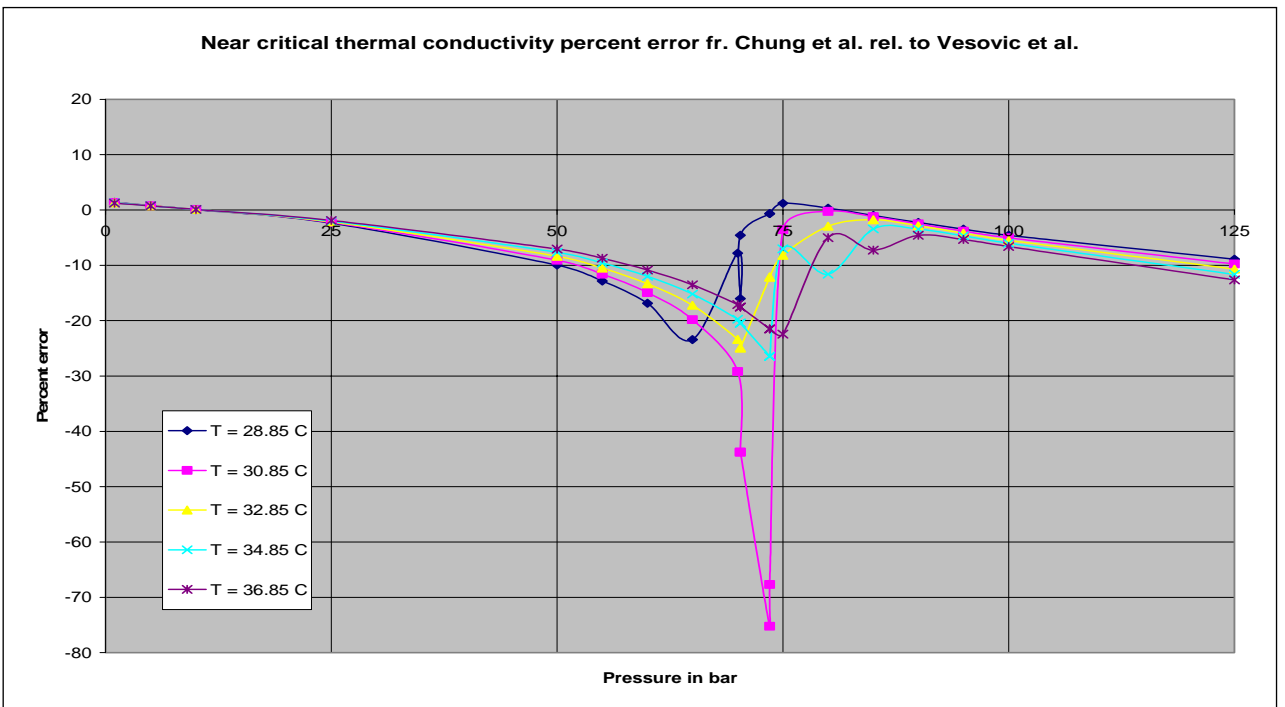


Fig. 3.2.9.9 CO₂ Thermal conductivity percent error near critical area from Chung et al.

Some points from Thermal conductivity graphs:

- The increase of pressure at constant temperature always increases the thermal conductivity while the increase of temperature at constant pressure may cause the thermal conductivity to increase or decrease depends on what “fluid behave” at that state. If the initial state is in liquid phase or “seems more to be liquid than gas” then the increase of temperature causes the decrease of thermal conductivity and the vice versa is valid which at gas phase, the increase of temperature increases the thermal conductivity. This behavior is similar to viscosity.
- At critical point, the thermal conductivity value is extremely high. Thus, it causes “shock wave” due to abrupt changes. The “strange” envelope is formed due to this high value of thermal conductivity where liquid saturation line bends up toward it. Gas saturation line jumps up away when it is close to critical point and these two lines meet at the critical point (It is not shown in the graph).
- TOTAL correlation to estimate saturated liquid thermal conductivity agrees well with the reference until the pressure of 70 bar (ca. 28 °C). TOTAL correlation to estimate saturated vapor thermal conductivity is a bit underestimate compared to the reference.
- The three methods used in this work show the consistent trend but deviation still exist. Chung method tends to overestimate at high pressure while PVTsim seems to underestimate at high pressure and high temperature compared to the reference.
- Below is the table of thermal conductivity percent error at area of interest and near critical area:

Method	Thermal Cond. percent error		Thermal Cond. percent error	
	Area of interest		Near critical area	
	Min.	Max.	Min.	Max.
Chung et al.	-25	15	-75	3
PVTsim	-20	5		

Table 3.2.9.1 CO₂ Thermal Conductivity percent error

3.2.10.1 CO₂ Joule-Thomson coefficient-Temperature plot

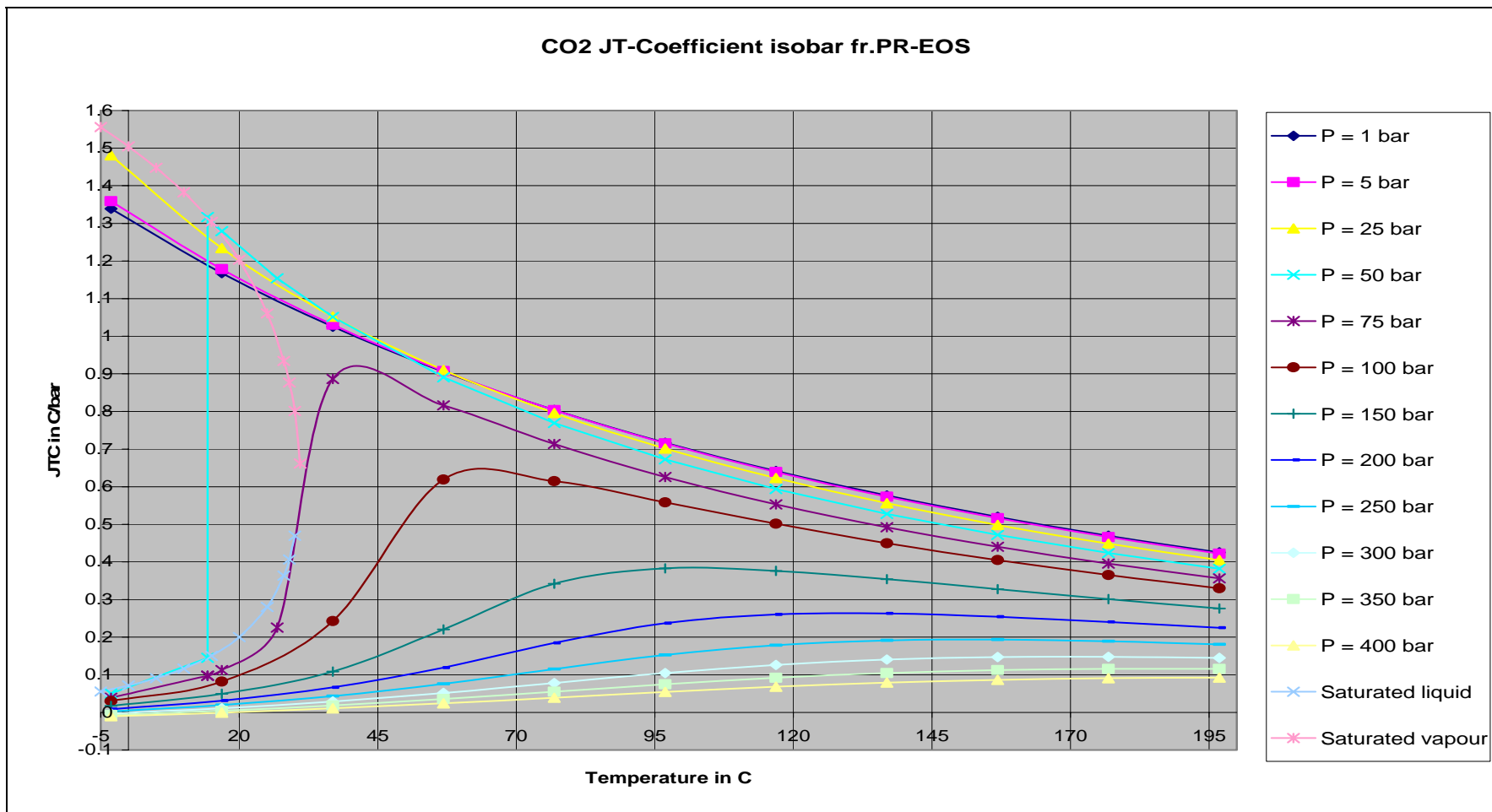


Fig. 3.2.10.1 CO₂ Joule-Thomson coefficient-Temperature plot (obtained from PR-EOS)

3.2.10.2 Comparison of CO₂ Joule-Thomson coefficient

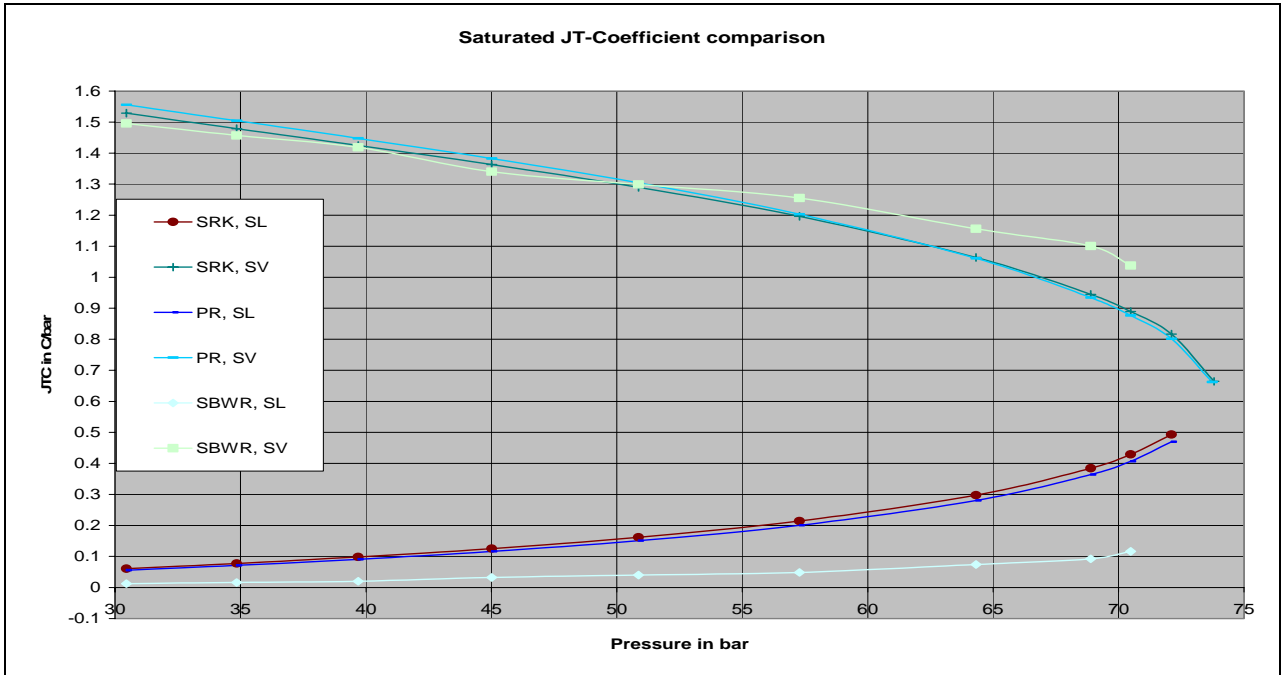


Fig. 3.2.10.2 Saturated CO₂ JT-coefficient comparison

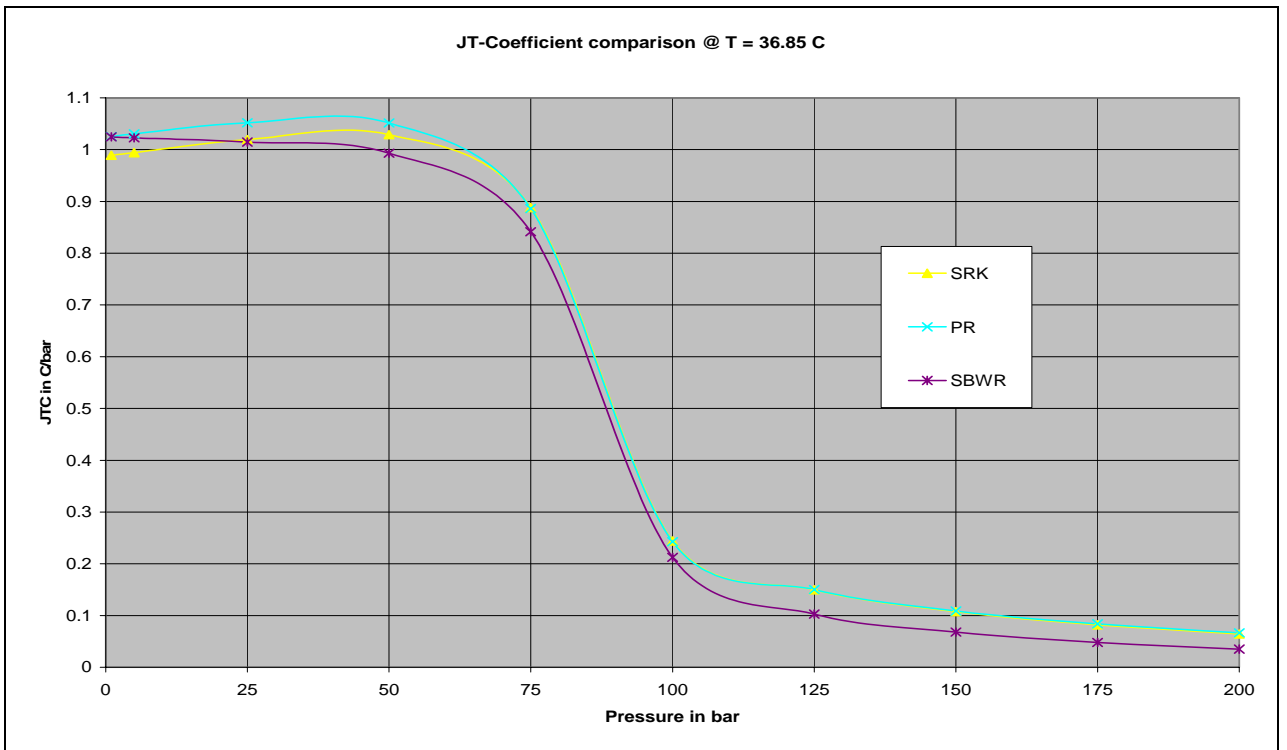


Fig 3.2.10.3 CO₂ JT-coefficient comparison at T = 36.85 °C

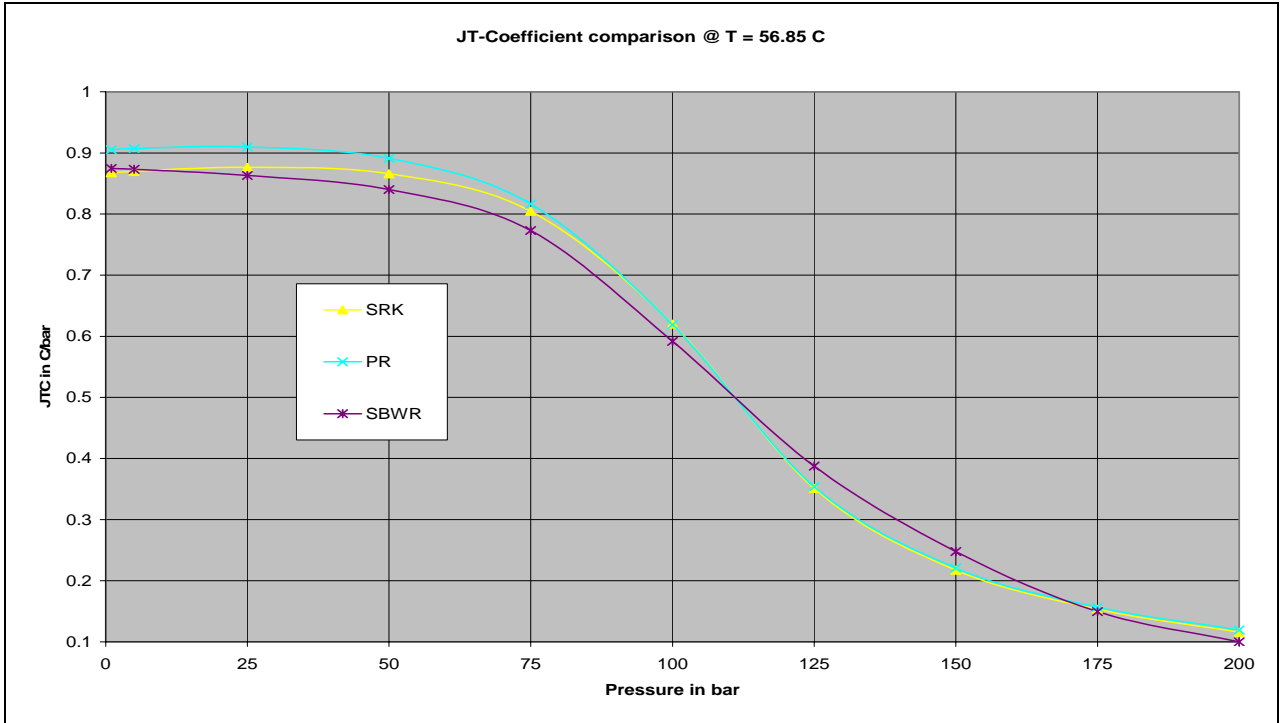


Fig 3.2.10.4 CO₂ JT-coefficient comparison at T = 56.85 °C

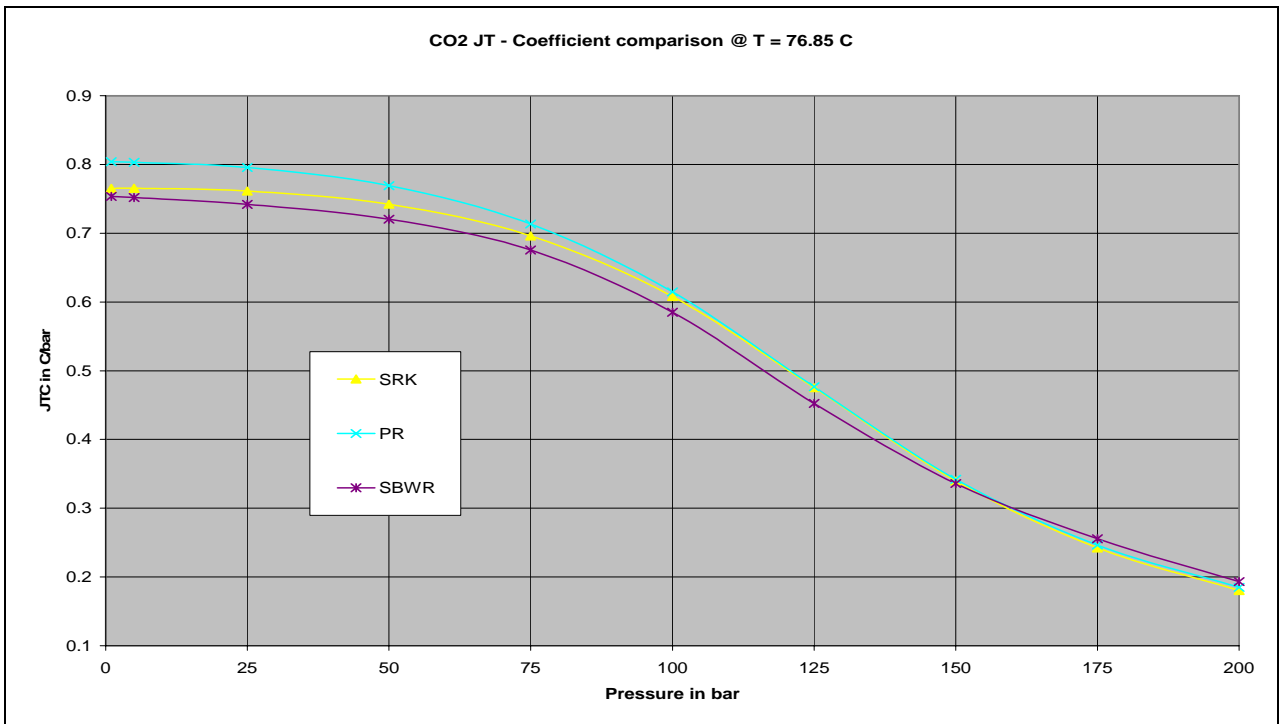


Fig 3.2.10.5 CO₂ JT-coefficient comparison at T = 76.85 °C

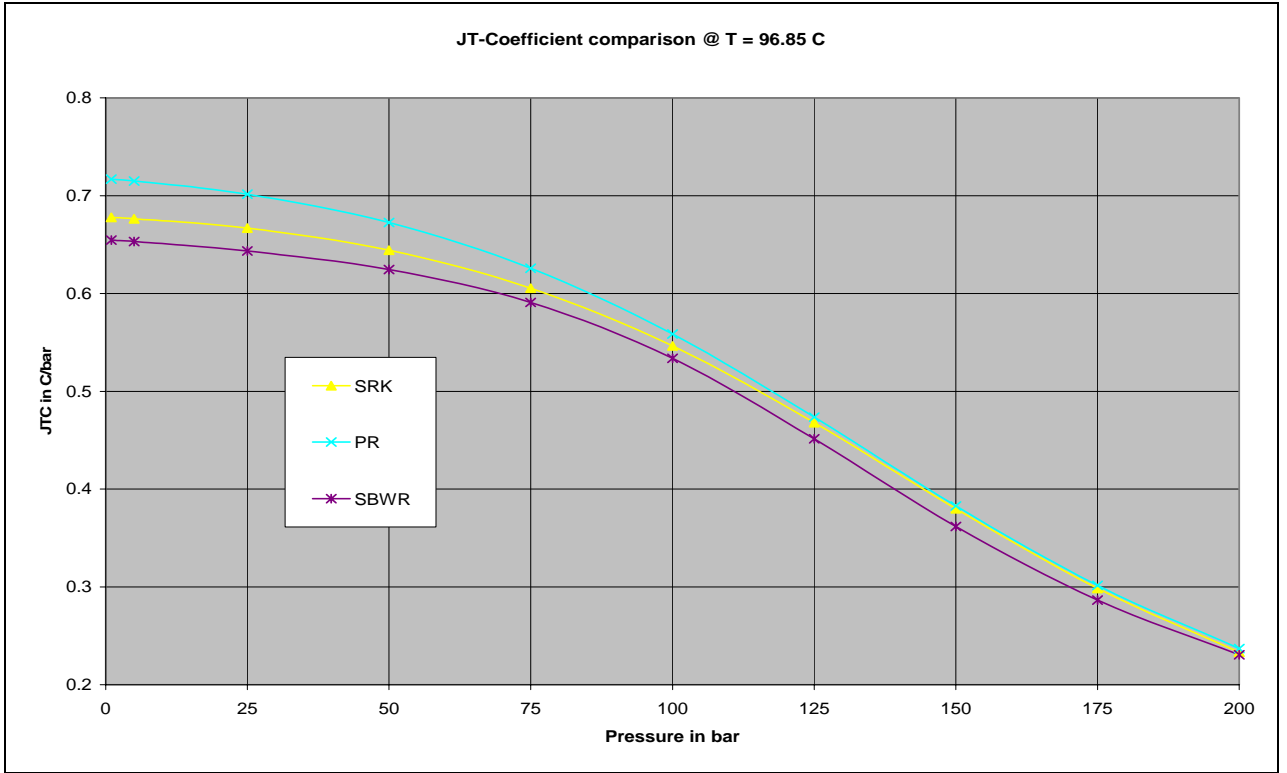


Fig 3.2.10.6 CO₂ JT-coefficient comparison at T = 96.85 °C

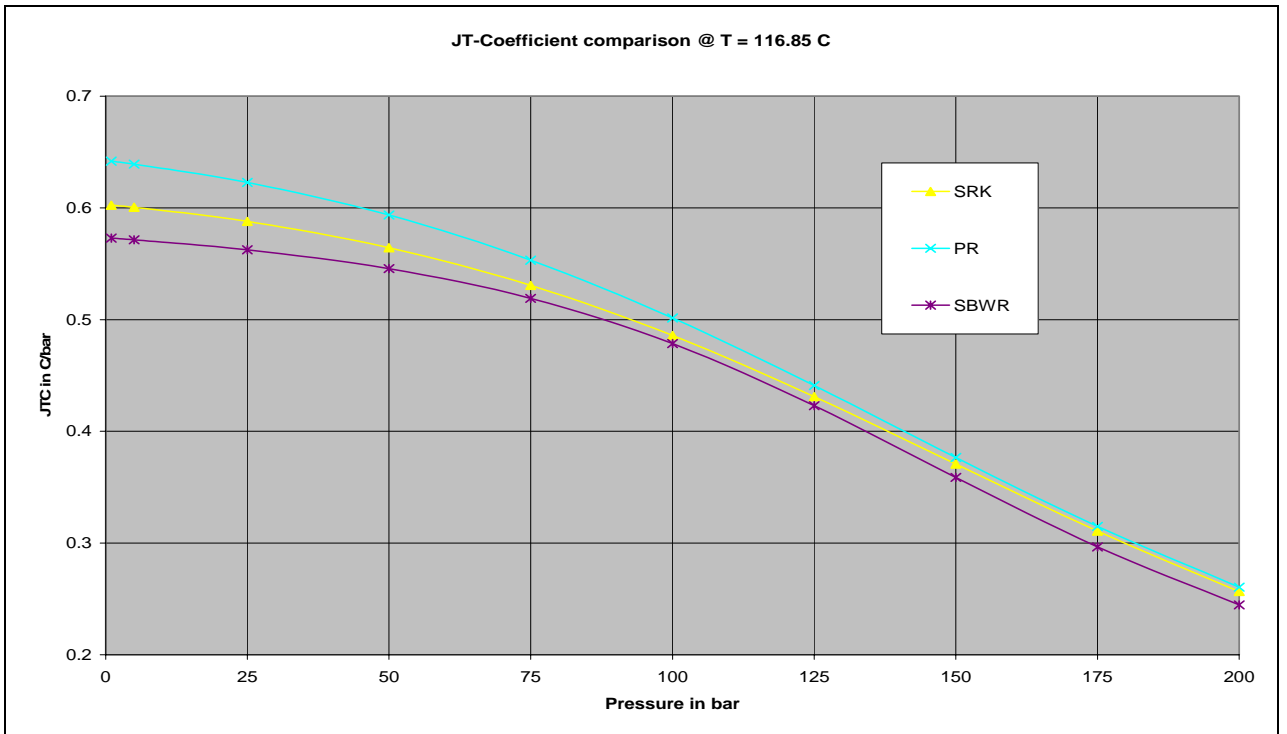


Fig 3.2.10.7 CO₂ JT-coefficient comparison at T = 116.85 °C

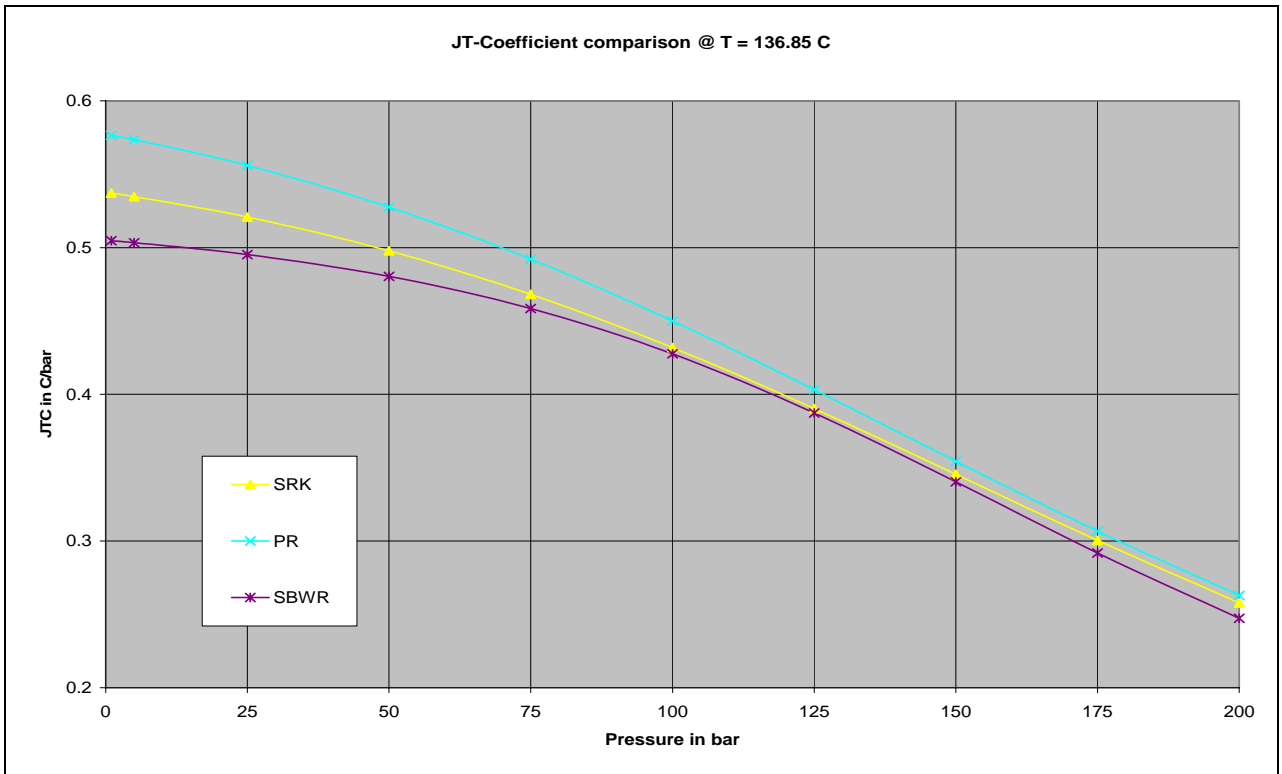


Fig 3.2.10.8 CO₂ JT-coefficient comparison at T = 136.85 °C

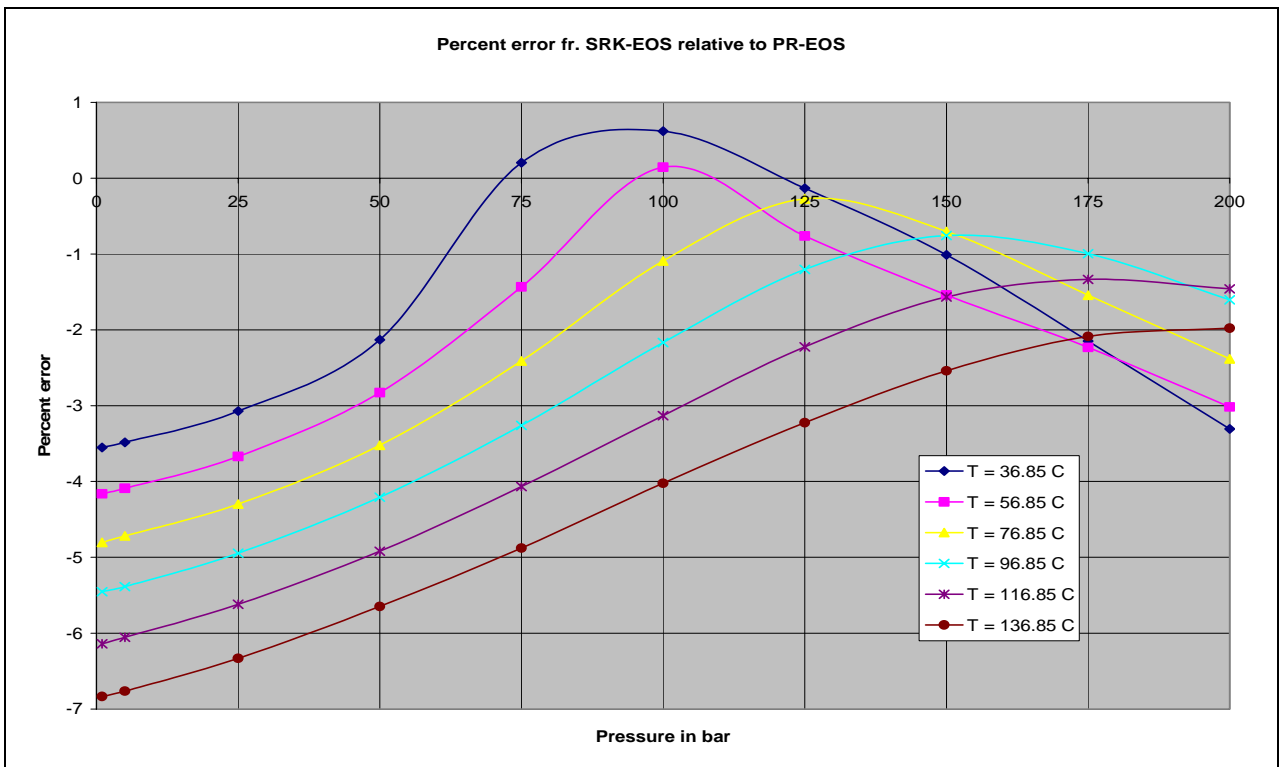


Fig 3.2.10.9 CO₂ JT-coefficient percent error at area of interest from SRK-EOS

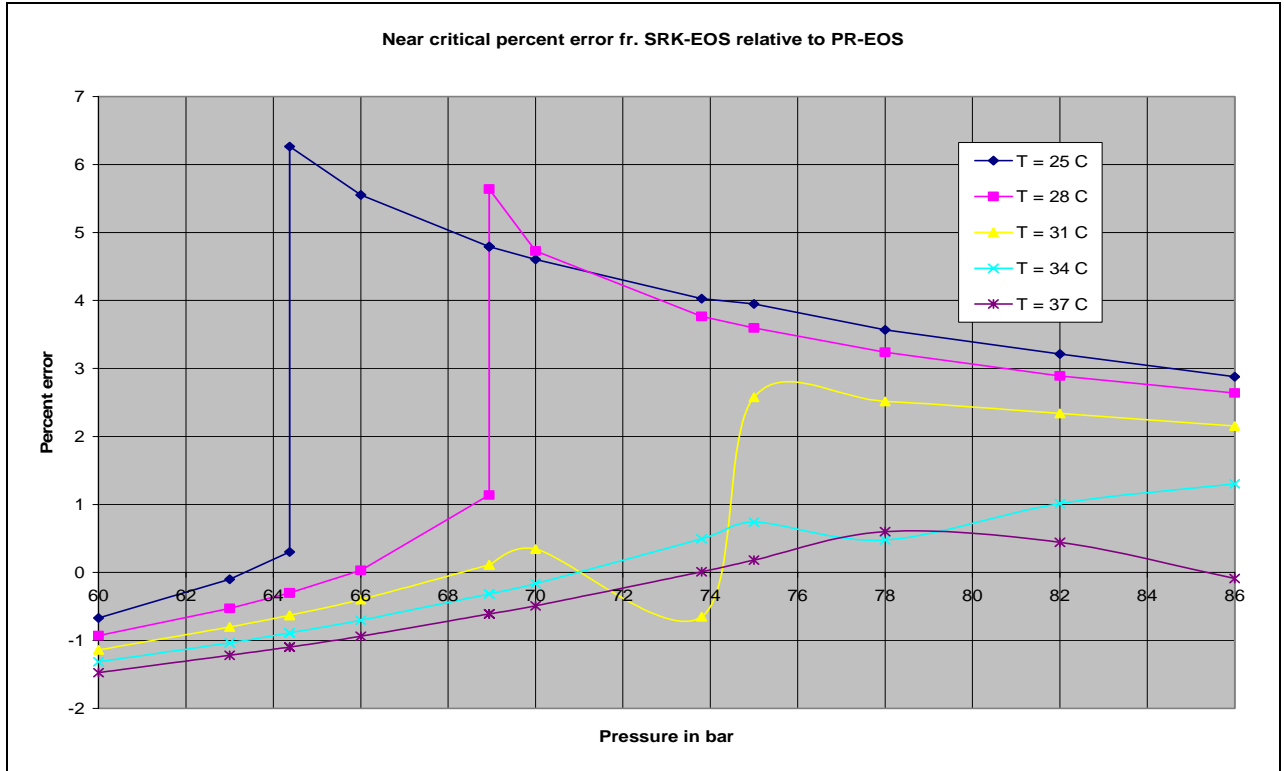


Fig 3.2.10.10 CO₂ JT-coefficient percent error near critical area from SRK-EOS

Some points from Joule-Thomson coefficient above:

- For gas phase, the increase of temperature at constant pressure causes the JT-coefficient to decrease. For liquid phase, the increase of temperature at constant pressure causes the JT-coefficient to increase. For others state, it depends on how the fluid likely to behave, if the fluid behave more to liquid phase then the JT-coefficient will increase when the temperature increase at constant pressure and will decrease if the fluid behaves more likely to gas phase.
- At the area near critical point, the change of JT-coefficient is significant due to the change of pressure and/or temperature. The change of JT-coefficient is more rapid on the gas phase than liquid phase.
- The large variation of JT-coefficient occurs at low pressure then tends to converge at high pressure. It is alleged that at high pressure and high pressure the JT-coefficient estimated by each EOS will result in the same value. But to be sure, the advance researches are needed.

- Below is the table of JT-coefficient percent error at area of interest and near critical region:

Method	JT-coeff. percent error		JT-coeff percent error	
	Area of interest		Near critical area	
	Min.	Max.	Min.	Max.
Starling-BWR	-50	15	-85	100
Soave-Redlich-Kwong	-7	1	-2	7

Table 3.2.10.1 CO₂ JT-coefficient percent error

The reference for percent error above is Peng-Robinson equation. We don't have more sources of this property which we can "trust" more to be the reference. Since all of our calculations are based on Peng-Robinson equation of state, we choose it as our reference for this property.

3.2.11.1 CO₂ Temperature-Entropy (T-S) diagram

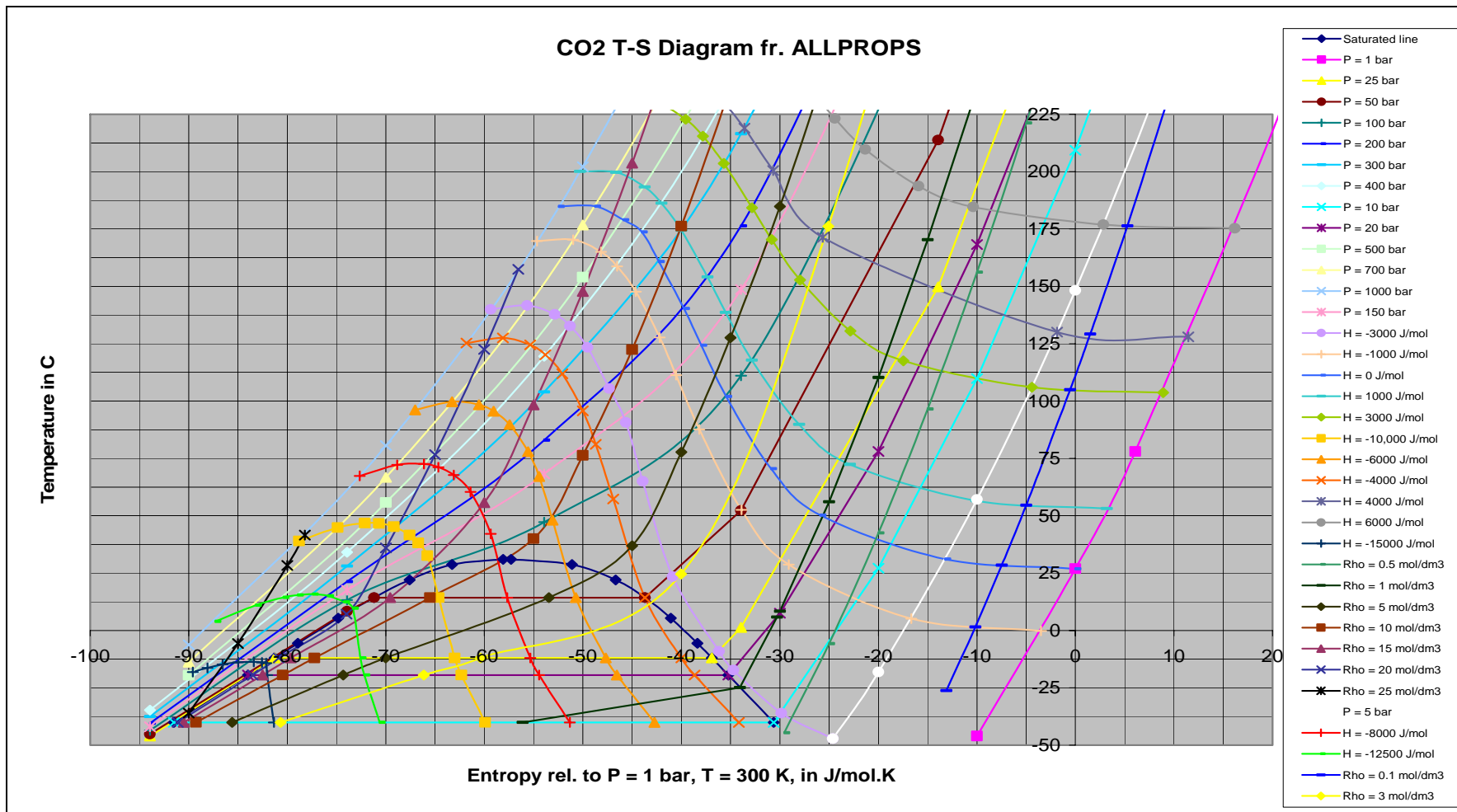


Fig. 3.2.11 CO₂ Temperature-Entropy diagram (obtained from ALLPROPS)

3.2.11.2 Example of the use of T-S Diagram

Problem:

We have CO₂ fluid with initial state of P = 50 bara and T = 50 °C. What is:

1. The temperature if we expand the fluid until the end pressure, P_{end} = 30 bara with constant enthalpy process?
2. The temperature if we expand the fluid until the end pressure, P_{end} = 30 bara with constant entropy process?
3. The enthalpy if we heat the fluid with constant pressure process until the end temperature T_{end} = 70 °C?
4. The entropy if we compress the fluid with isothermal process until the end pressure P_{end} = 70 bara?
5. The enthalpy and entropy change if the end state is P = 60 bara and T = 60 °C?

Solution:

From CO₂ T-S Diagram (datum: 1 bara, 300 K), the initial state (50 °C, 50 bara) gives the corresponding enthalpy and entropy respectively: -1150 J/mole and -34.34 J/mole.K

1. By following isenthalpy line of -1150 J/mole from the initial state to the point where the corresponding pressure is 30 bara, we get end temperature: T_{end} = 30.95 C
2. By following isentropy line (i.e. vertical line) of -34.34 J/mole.K from initial state to the point where the corresponding pressure is 30 bara, we get end temperature: T_{end} = 11.88 °C
3. By following isobar line of 50 bara from initial state to the point where the corresponding temperature is 70 °C, we get end enthalpy: H_{end} = -27 J/mole
4. By following isothermal line (i.e. horizontal line) of 50 °C from initial state to the point where the corresponding pressure is 70 bara, we get end entropy: S_{end} = -40.09 J/mole.K
5. The end state (60 °C, 60 bara) gives the corresponding enthalpy and entropy respectively: -1046 J/mole and -35.2 J/mole.K. Thus the enthalpy and entropy change are 104 J/mole and -0.86 J/mole.K

3.3 Hydraulics Results and Discussion

3.3.1 Isothermal Static Pressure distribution

The base case for this scenario is

Temperature: 50 °C

Surface pressure: 30 bara

The length of vertical pipe: 5200 meters

Diameter of pipe: 3.5 inches

The calculation is done based on segment length 25 m, variable gravity acceleration, using PR-EOS in calculation and temperature is set constant of 50 °C along the pipe.

Sensitivity analysis:

- The length of pipe segment: 12.5 m, 50m, 100m
- Equation of state used for calculation: SRK-EOS, SBWR-EOS
- Temperature: 40 °C, 60 °C, 100 °C
- Surface pressure: 20 bara, 40 bara, 100 bara
- Pipe diameter: 4 inches, 5 inches
- Gravitation: constant gravity

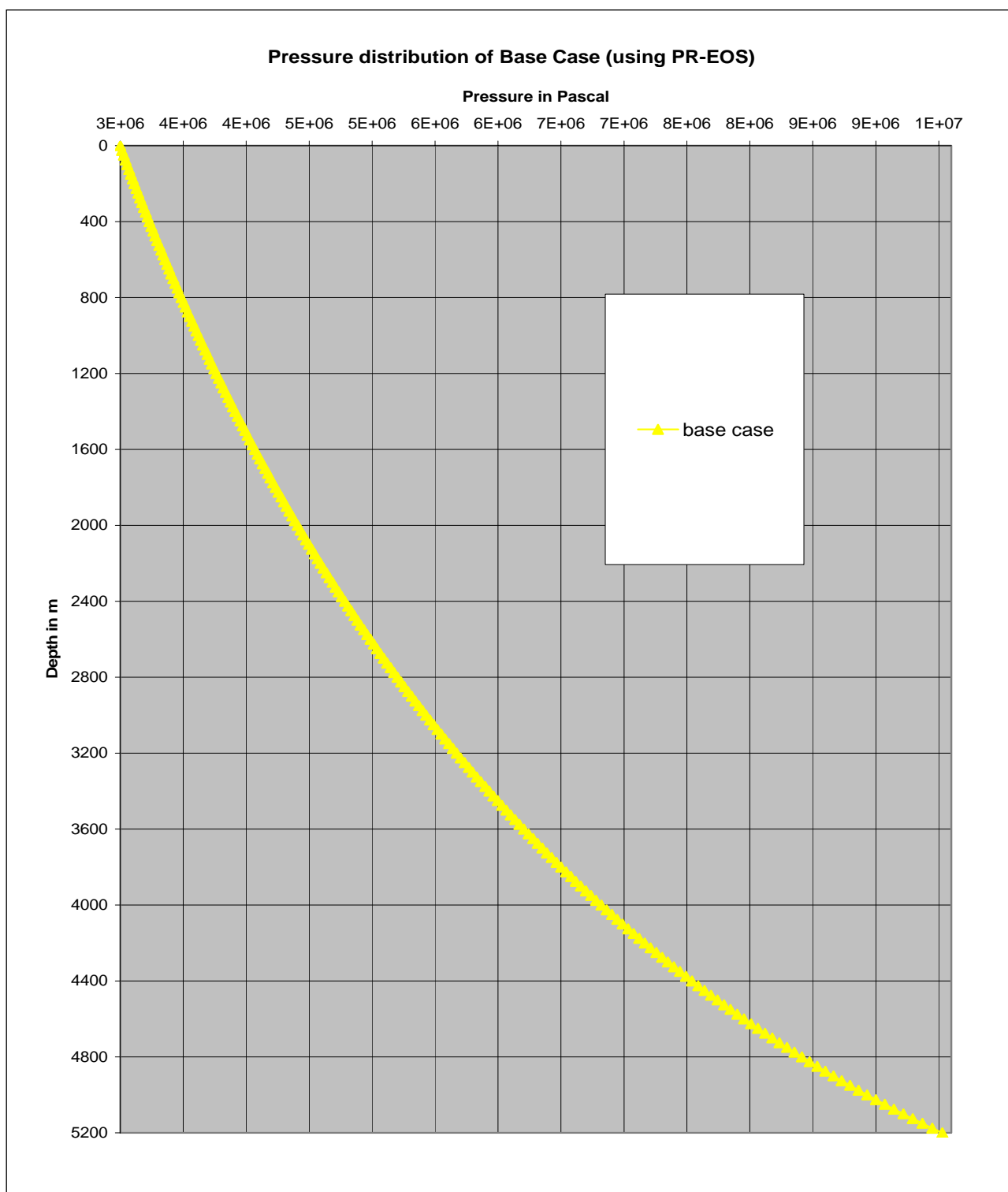


Fig. 3.3.1.1 Base case static pressure profile

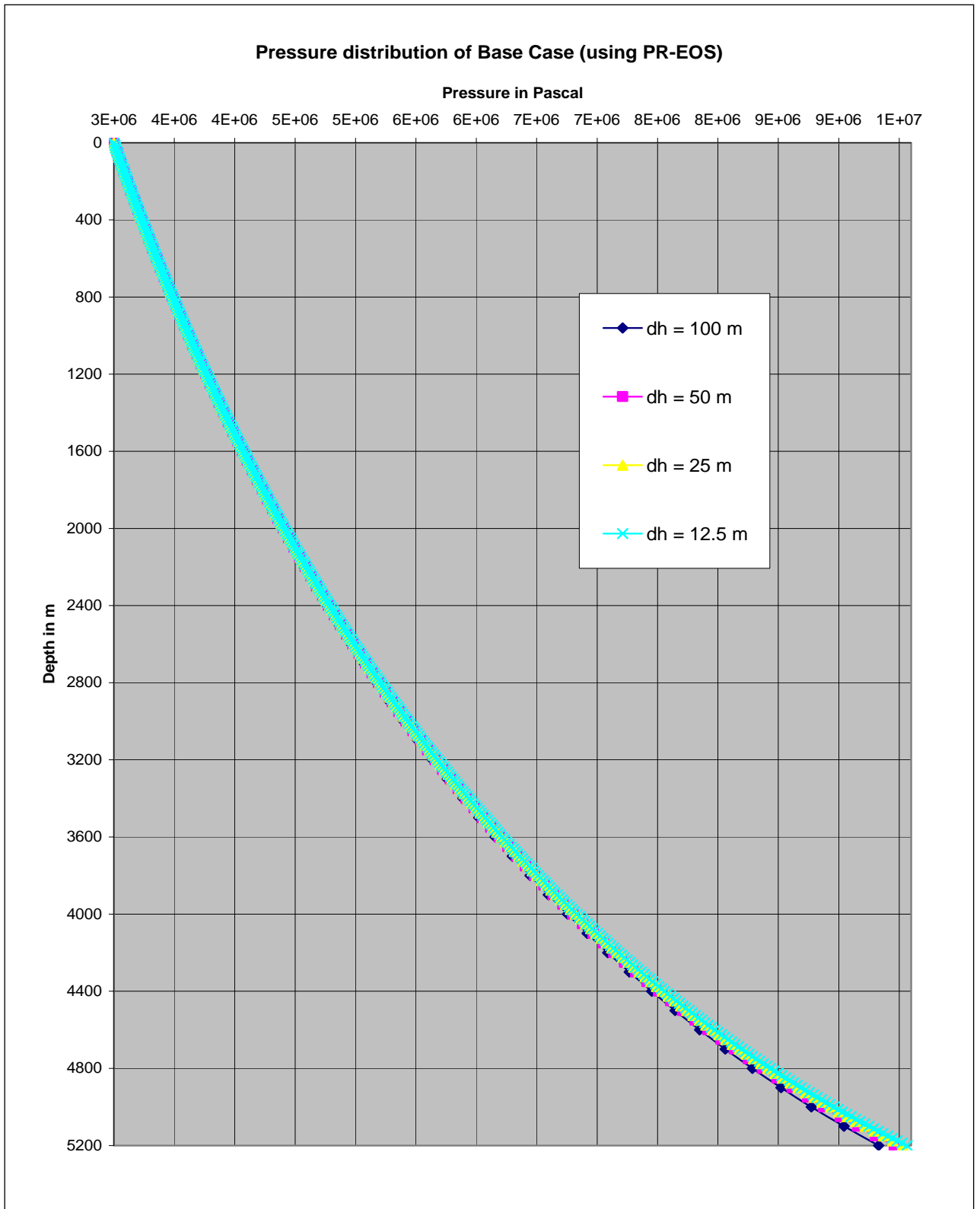


Fig. 3.3.1.2 Pressure sensitivity due to the length of pipe segment for isothermal static scenario

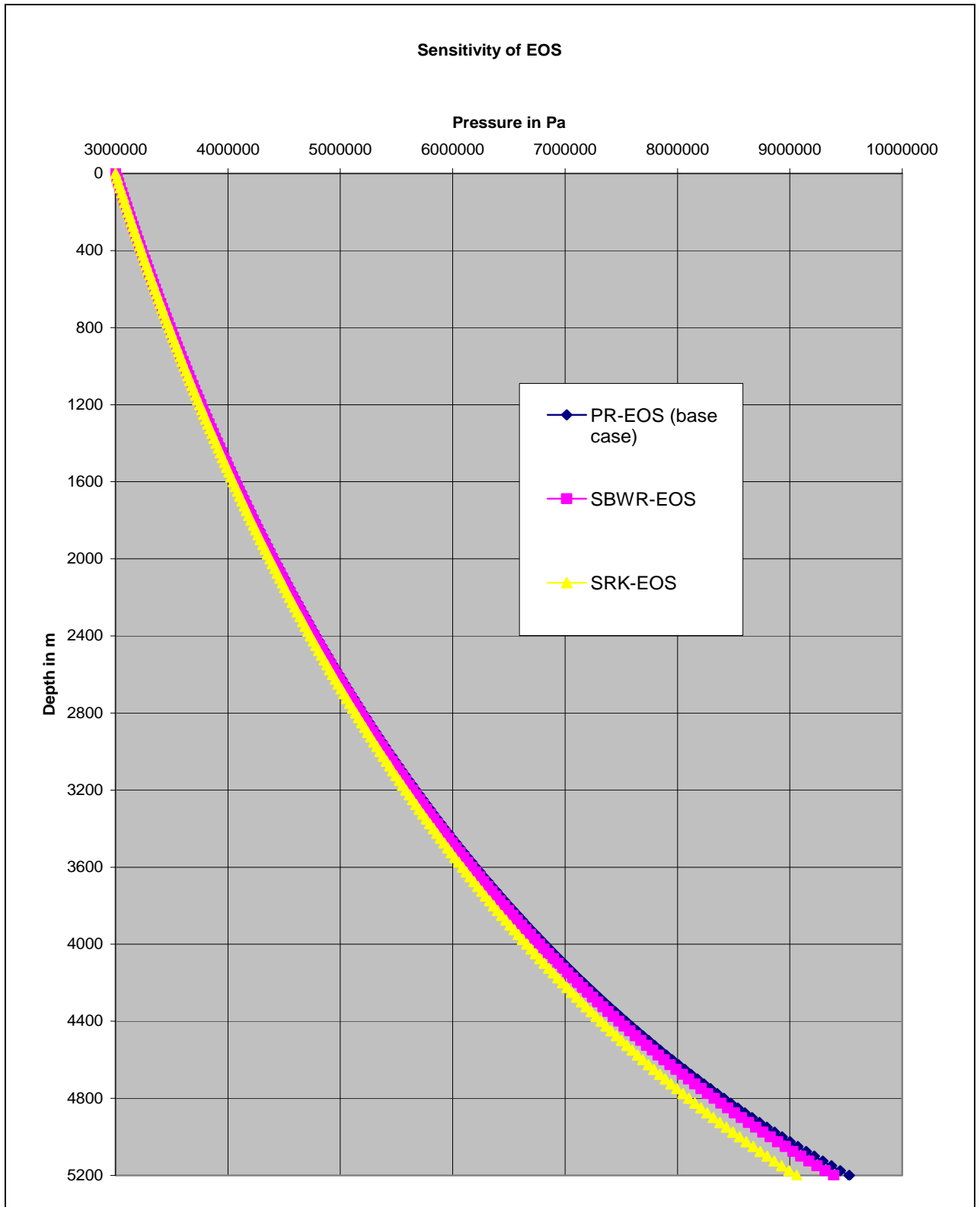


Fig. 3.3.1.3 Pressure sensitivity due to the EOS used in the calculation for isothermal static scenario

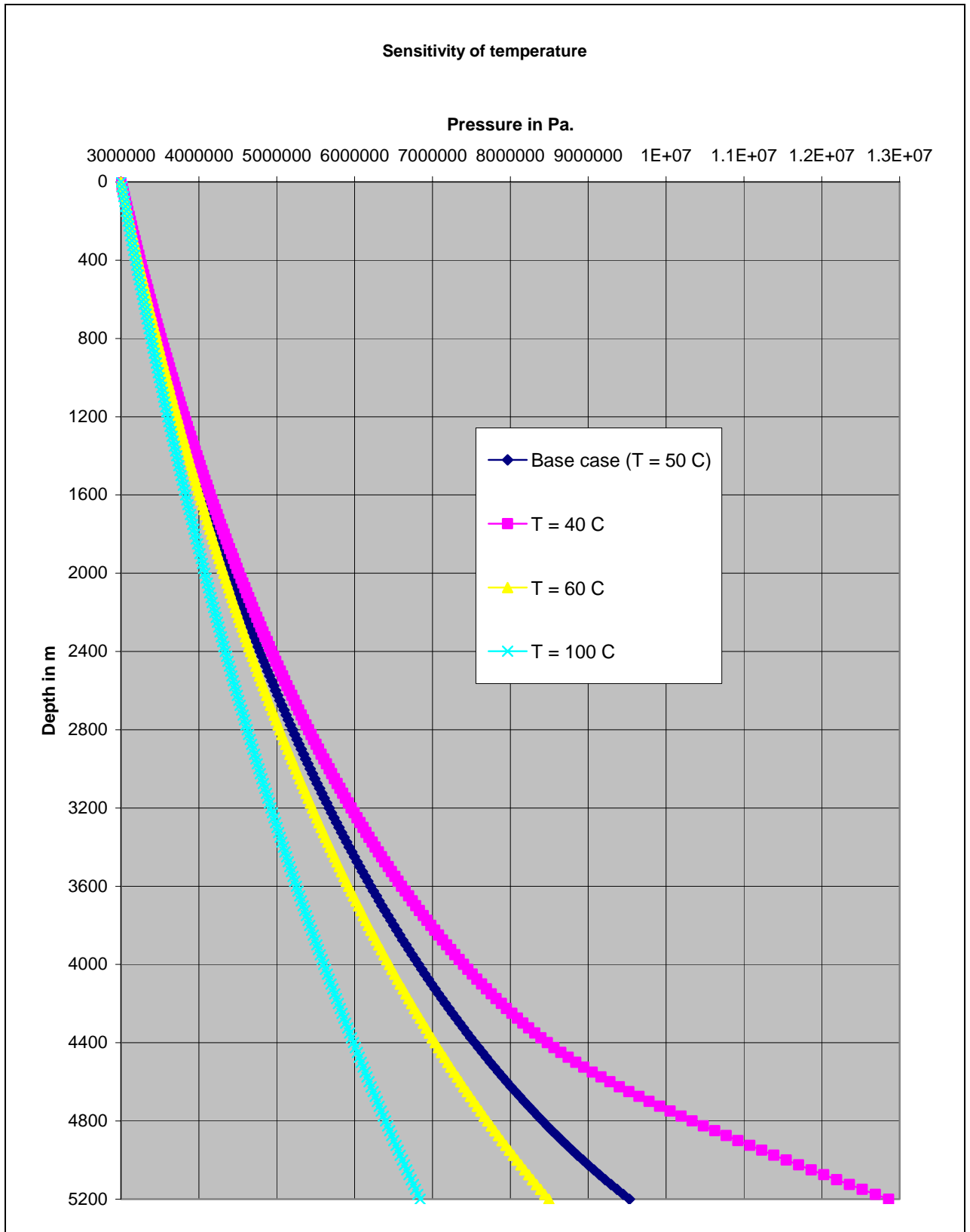


Fig. 3.3.1.4 Pressure sensitivity due to temperature for isothermal static scenario

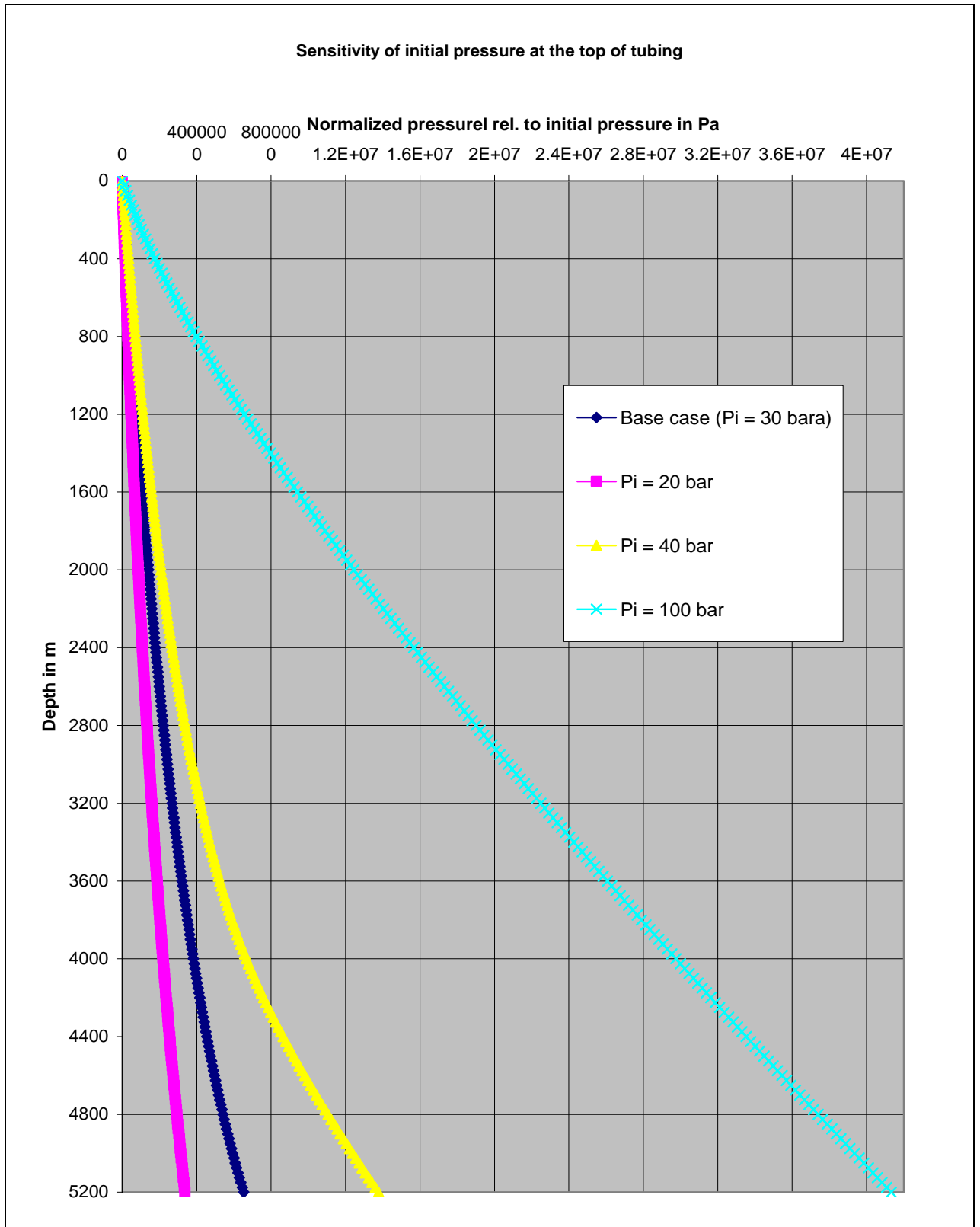


Fig. 3.3.1.5 Pressure sensitivity due to the surface pressure for isothermal static scenario

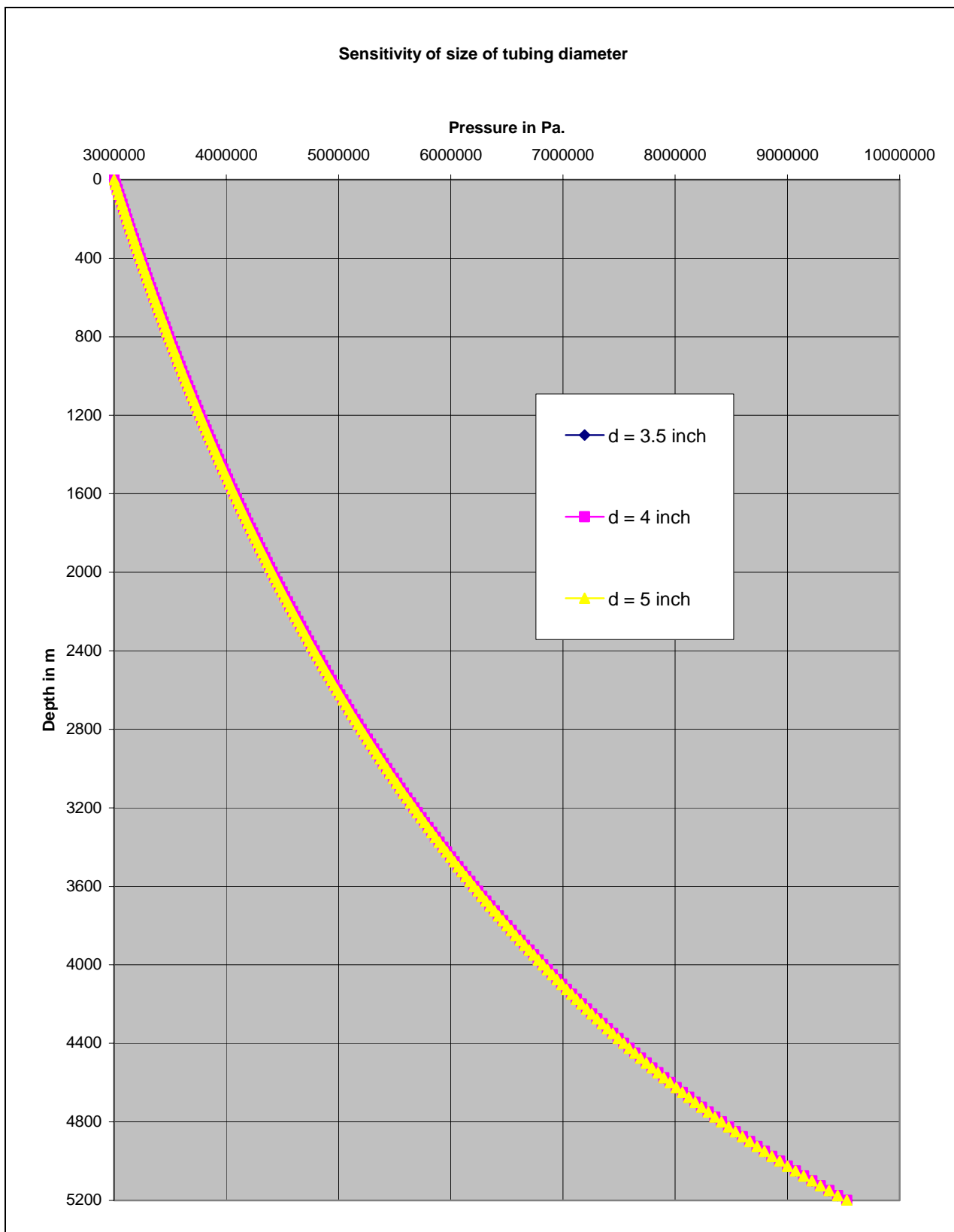


Fig. 3.3.1.6 Pressure sensitivity due to the pipe diameter for isothermal static scenario

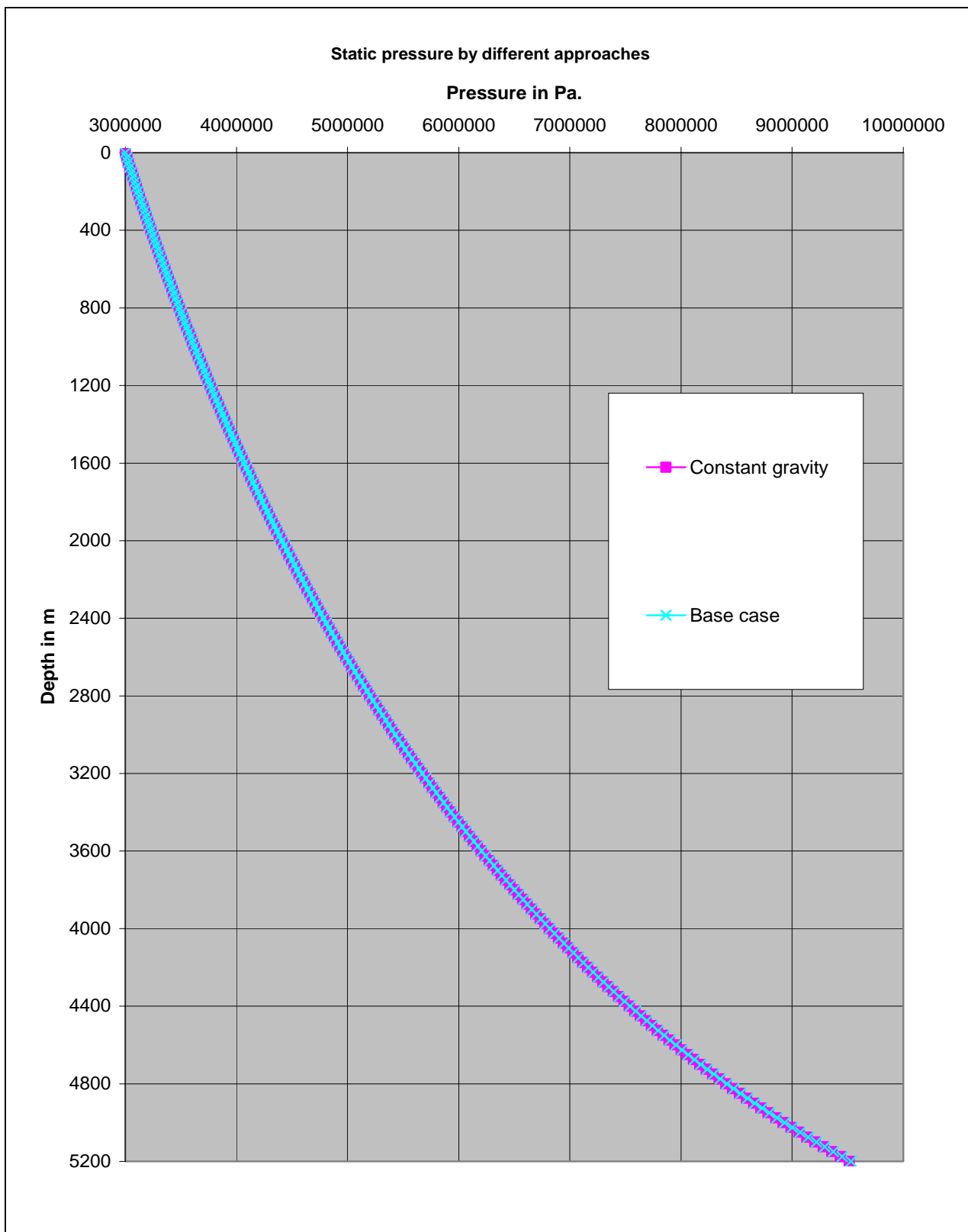


Fig. 3.3.1.7 Pressure sensitivity due to the pipe diameter for isothermal static scenario

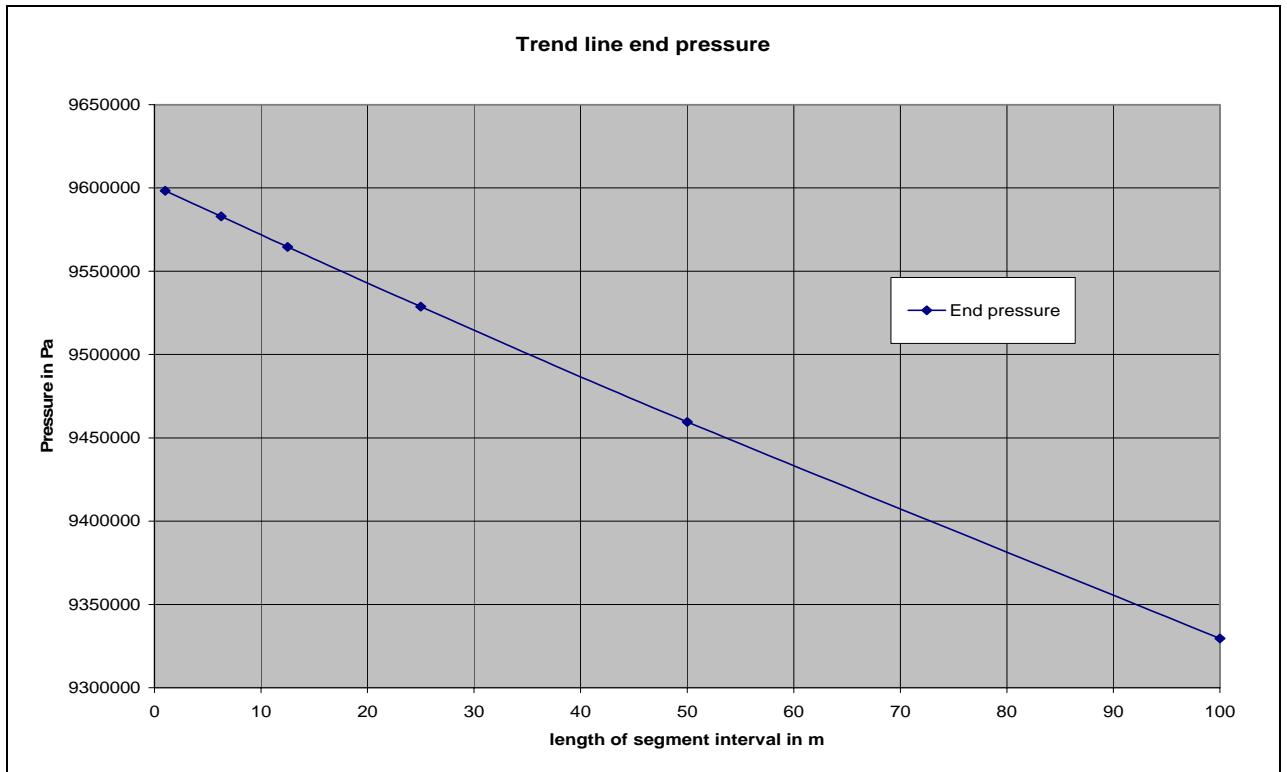


Fig. 3.3.1.8 Plot of end pressure with respect to the length of pipe segment

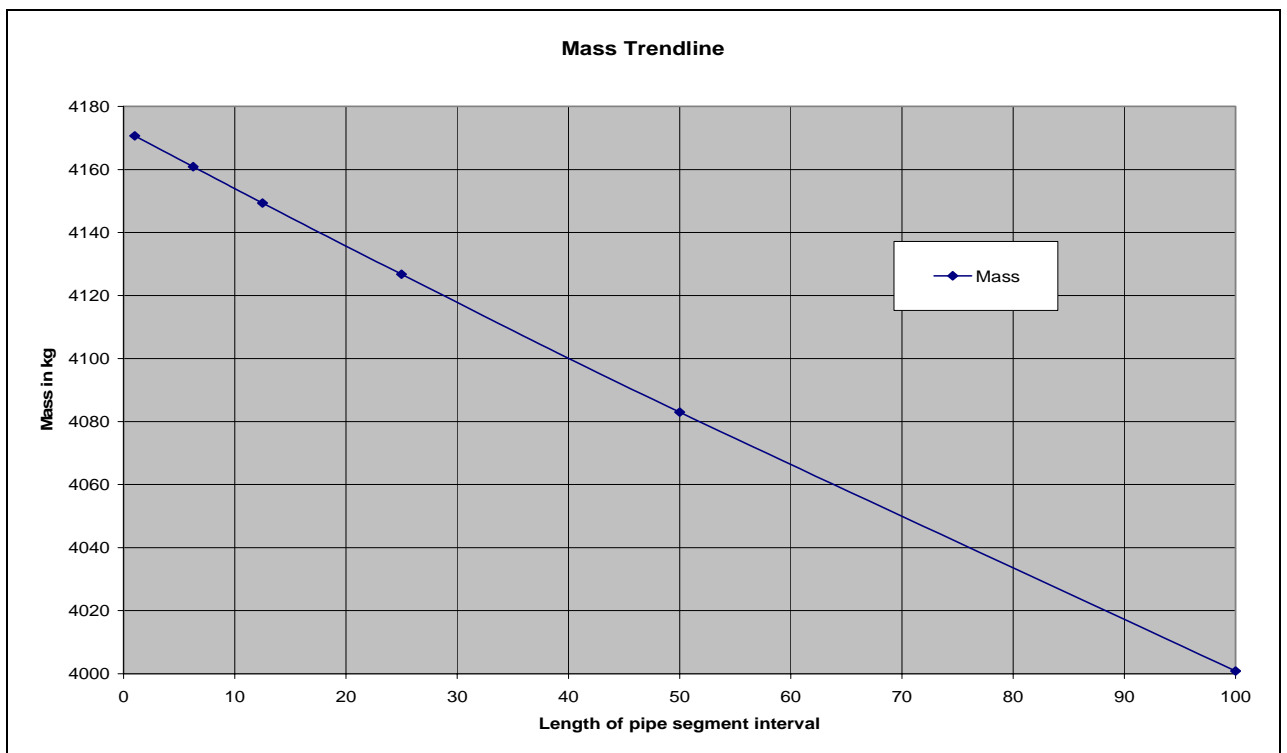


Fig. 3.3.1.9 Plot of the total mass in the pipe with respect to pipe segment length

If we only concern to the initial and the end point of the segment, all graphs above can be summarized in the table below:

Injection case	Pressure		Total mass (kg)
	Top(bara)	Bottom (bara)	
Base case	30	95.288	4126.73
Pipe segment length = 12.5m	30	95.648	4149.38
Pipe segment length = 50m	30	94.595	4082.96
Pipe segment length = 100m	30	93.296	4000.85
SRK-EOS	30	90.603	3830.67
SBWR-EOS	30	93.9	4079.94
Temperature = 40 C	30	128.585	6230.62
Temperature = 60 C	30	84.933	3472.36
Temperature = 100 C	30	68.414	2428.3
Top pressure = 20 bara	0*	33.729*	2132.06
Top pressure = 40 bara	0*	137.735*	8705.13
Top pressure = 100 bara	0*	413.32*	26128.61
Diameter = 4 inches	30	95.288	5390.02
Diameter = 5 inches	30	95.288	8421.91
Constant gravity	30	95.152	4122.41

Table 3.3.1 Summary of sensitivity analysis of isothermal static pressure

The “star superscript” sign refers to normalized value (i.e. the pressure – the initial/top pressure)

Some points from the graphs above:

- Isothermal static pressure profile is not linear. Pressure gradient grows with the growth of depth. Fluid in very deep place is very high compressed and the density getting larger which causes pressure getting larger as well.
- The length of pipe segment influences the accuracy of the calculation. We observe that the bottom pressure increases insignificantly with the decrease of the pipe segment length. This is due to the shorter the pipe segment length, the more fluid density is “captured” in the calculation. The plot of bottom pressure and total mass in pipe versus the pipe segment length show the linearity relation between both. This relation is very useful because we can extrapolate to pipe segment

equal to zero. Theoretically, the pressure/mass at zero length of pipe segment is the “true” pressure/mass. If we want to have the “true” pressure/mass along the pipe then we can do this technique for every point in the pipe. Here, we only do it for the end pressure of the base case. The end pressure and mass for base case at zero length of pipe segment are 96.013 bara and 4172.54 kg.

- Equation of state used for calculation indeed influences the pressure distribution calculation. As mentioned in CO₂ property chapter, SRK-EOS tends to underestimate the density value and it is also seen in the pressure distribution which the pressure curve is under others from other EOS's. It means that the property behavior can explain the behavior of pressure and temperature distribution along the pipe with the fluid inside of it.
- High temperature causes the density to decrease. This statement explains why we have the lower pressure for higher isothermal temperature of the fluid along the pipe.
- The increase of surface pressure surely causes the increase of pressure at bottom of pipe. This increment is not linear. It means that we can't expect the linearity in estimating the bottom pressure based on two set of top-bottom pressure known.
- When the pressure high enough to make the state behave like liquid where the density changes insignificantly with the changes of pressure or in some case can be assumed constant, the profile of pressure along the pipe tends to be linear.
- The size of pipe diameter doesn't influence the static pressure profile.
- Gravity acceleration doesn't give significant change (i.e. very small) in pressure calculation along the pipe. For practical purpose, this gravity acceleration can be assumed constant in the calculation.
- The total mass of fluid in the pipe depends on the density along the pipe. Thus, density is the main key here to explain the behavior of static pressure profile in the pipe.

3.3.2 Steady State Isenthalpy flow

The base case for this scenario is

Surface injection temperature: 50 °C

Surface injection pressure: 30 bara

The length of vertical pipe: 5200 meters

Diameter of pipe: 3.5 inches

Mass rate injection: 2.15 kg/s

Pressure and temperature distribution are calculated based on pipe segment length of 25 m and using PR-EOS.

Sensitivity analysis (on pressure only):

- Pipe segment length: 12.5 m, 50 m, 100m
- Surface injection temperature: 40 °C, 60 °C, 100 °C
- Surface injection pressure: 20 bara, 40 bara, 100 bara
- Pipe diameter: 4 inches, 5 inches
- Injection mass rate: 0.5 kg/s, 5 kg/s

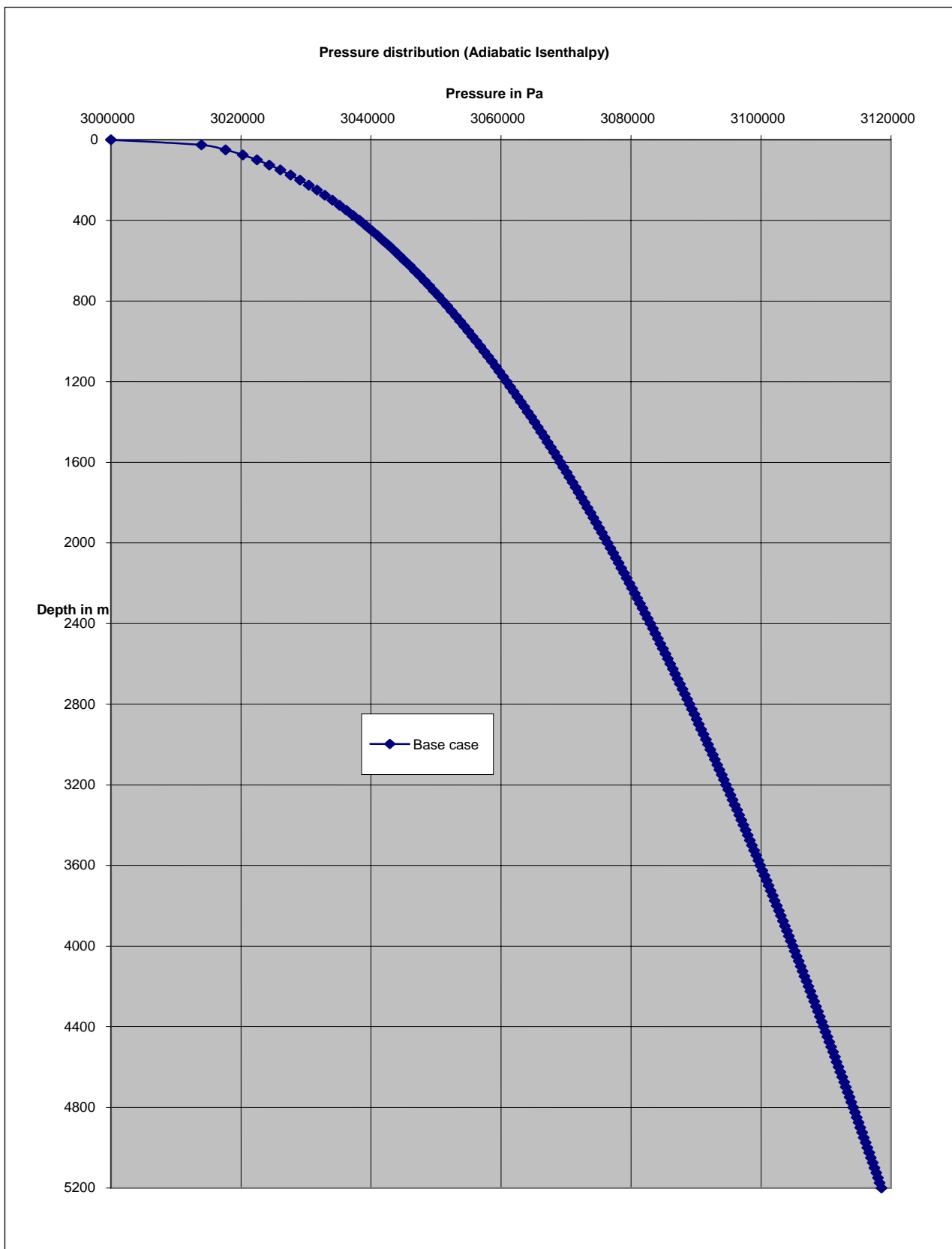


Fig. 3.3.2.1 Pressure profile of base case of steady state isenthalpy flow

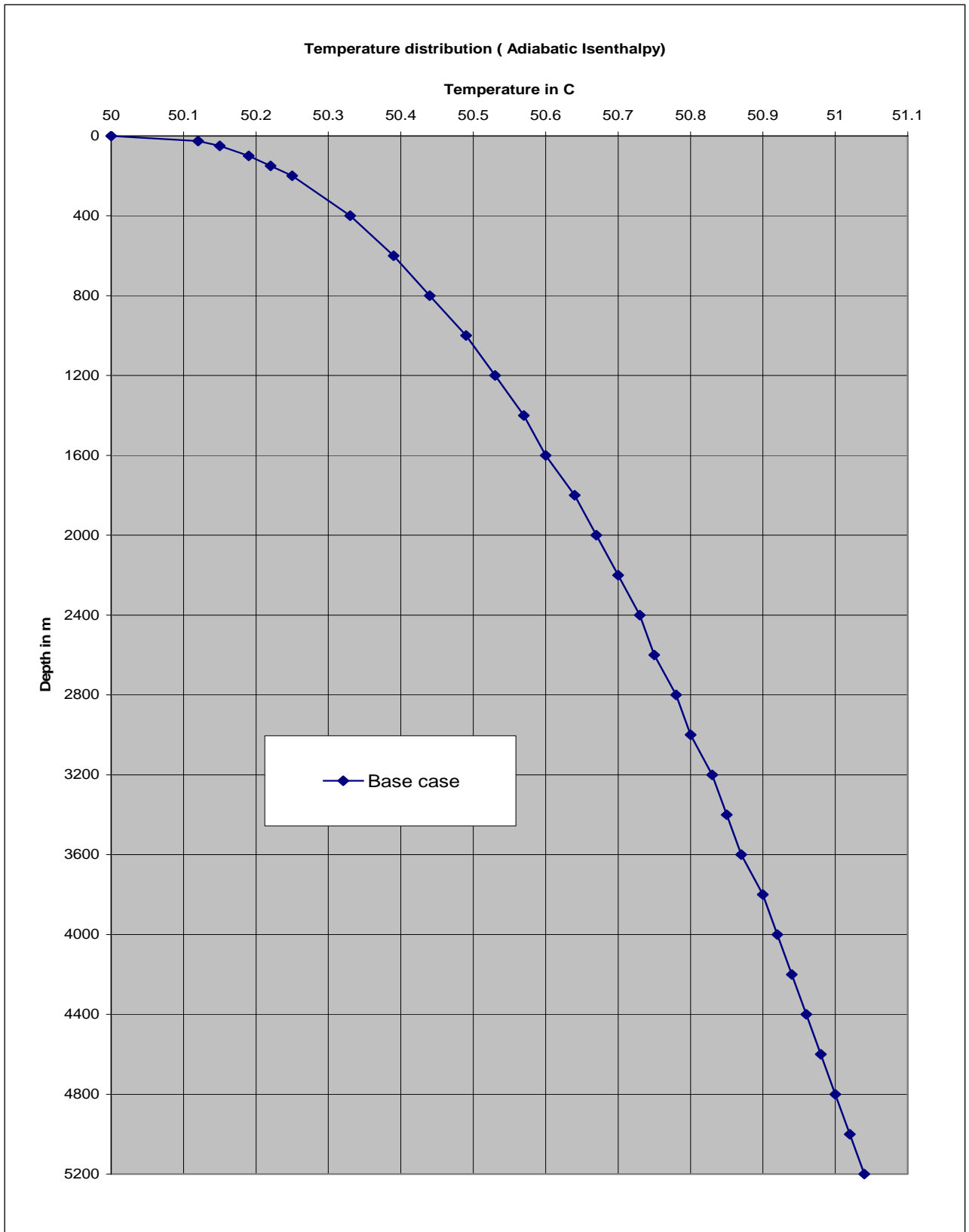


Fig. 3.3.2.2 Temperature profile of base case of steady state isenthalpy flow

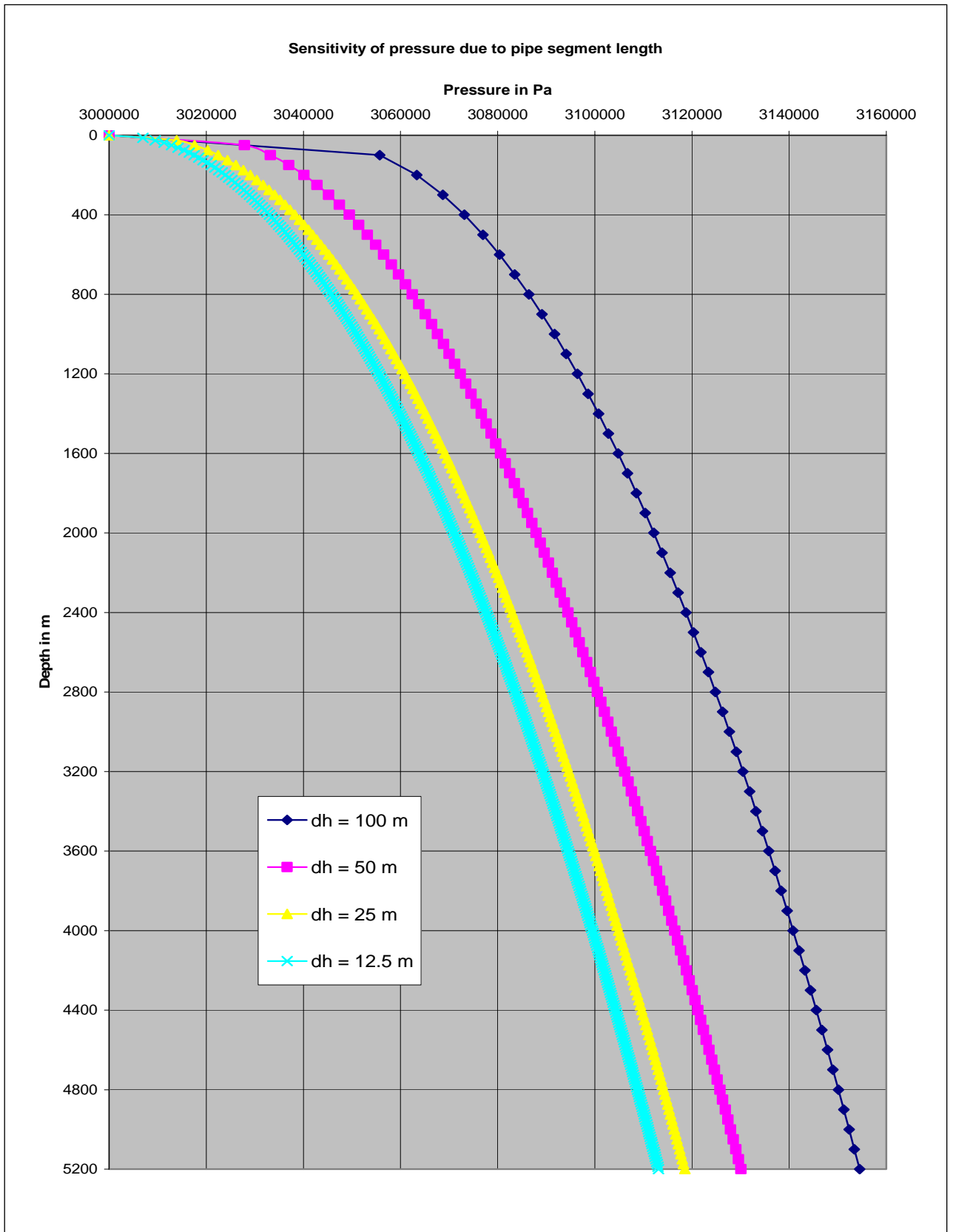


Fig. 3.3.2.3 Sensitivity due to length of pipe segment for isenthalpy flow

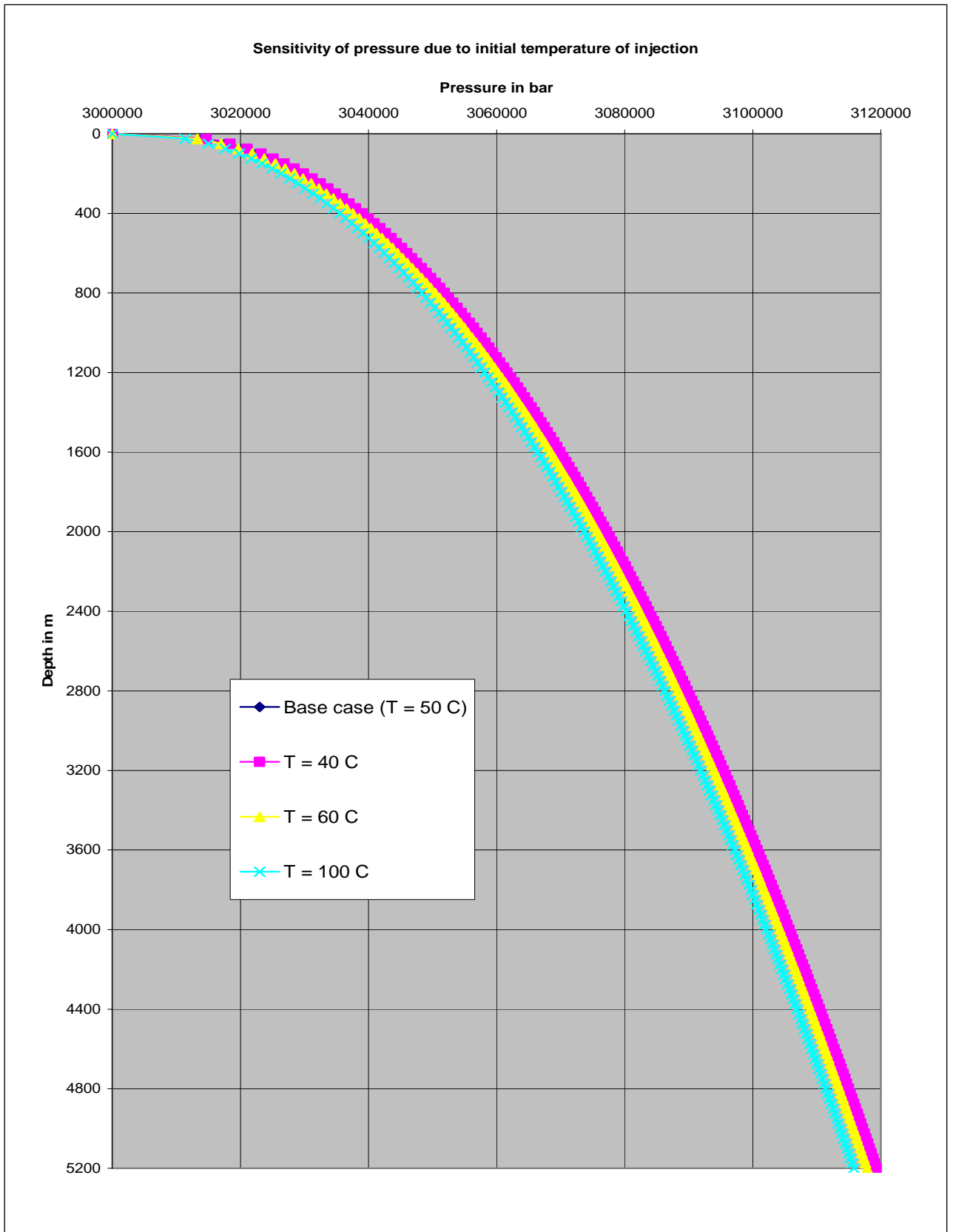


Fig. 3.3.2.4 Sensitivity due to surface injection temperature for isenthalpy flow

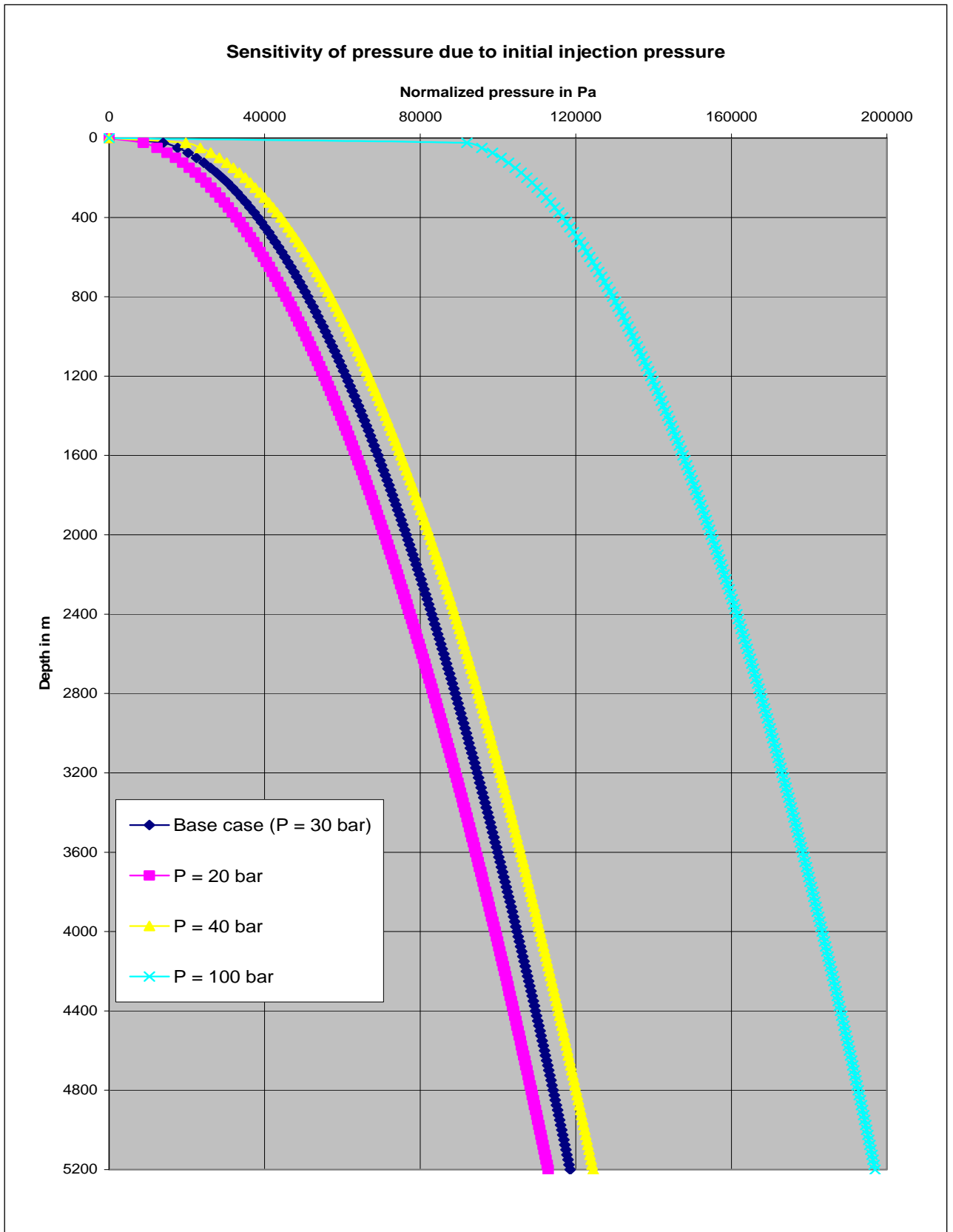


Fig. 3.3.2.5 Sensitivity due to surface injection pressure for isenthalpy flow

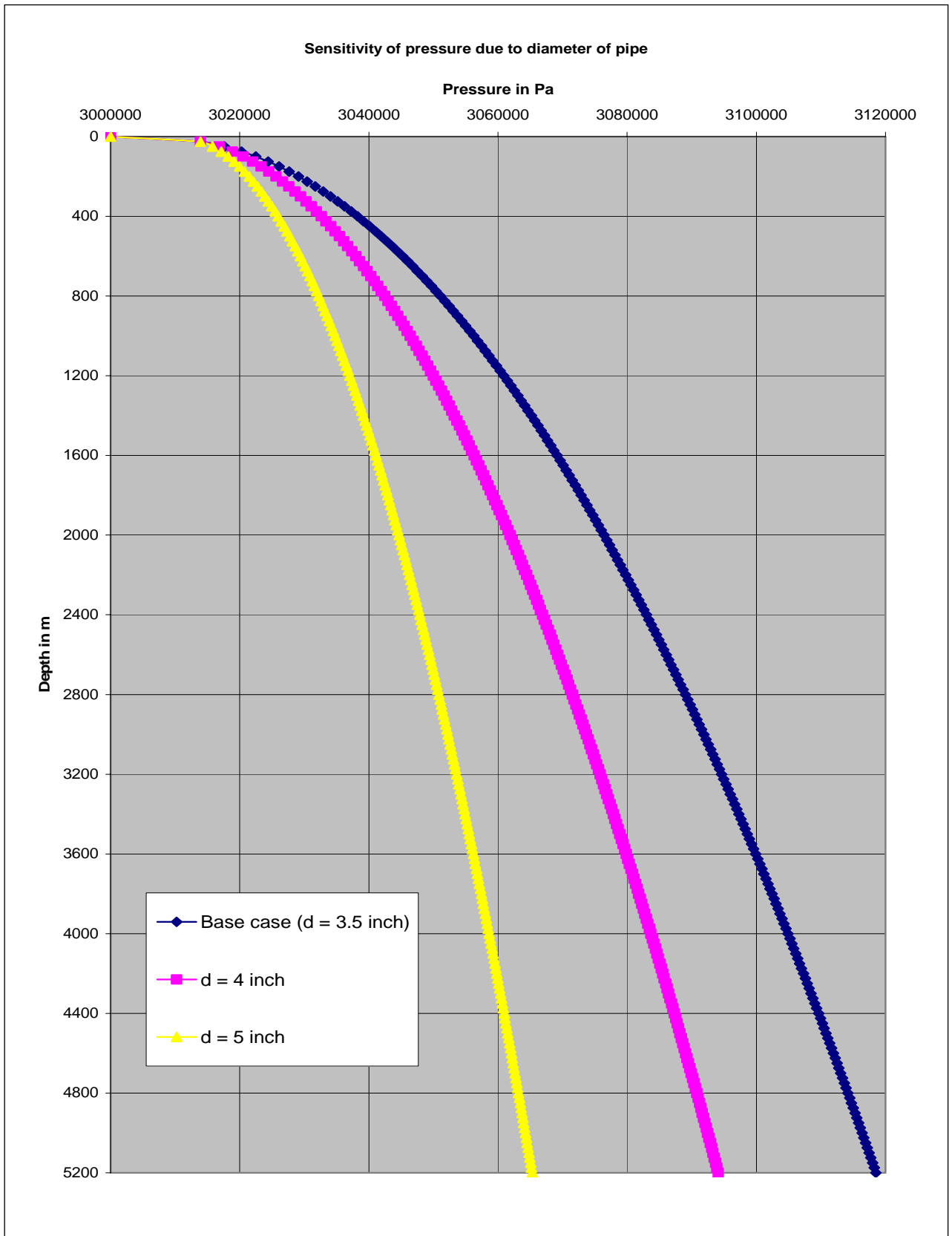


Fig. 3.3.2.6 Sensitivity due to size of pipe diameter for isenthalpy flow

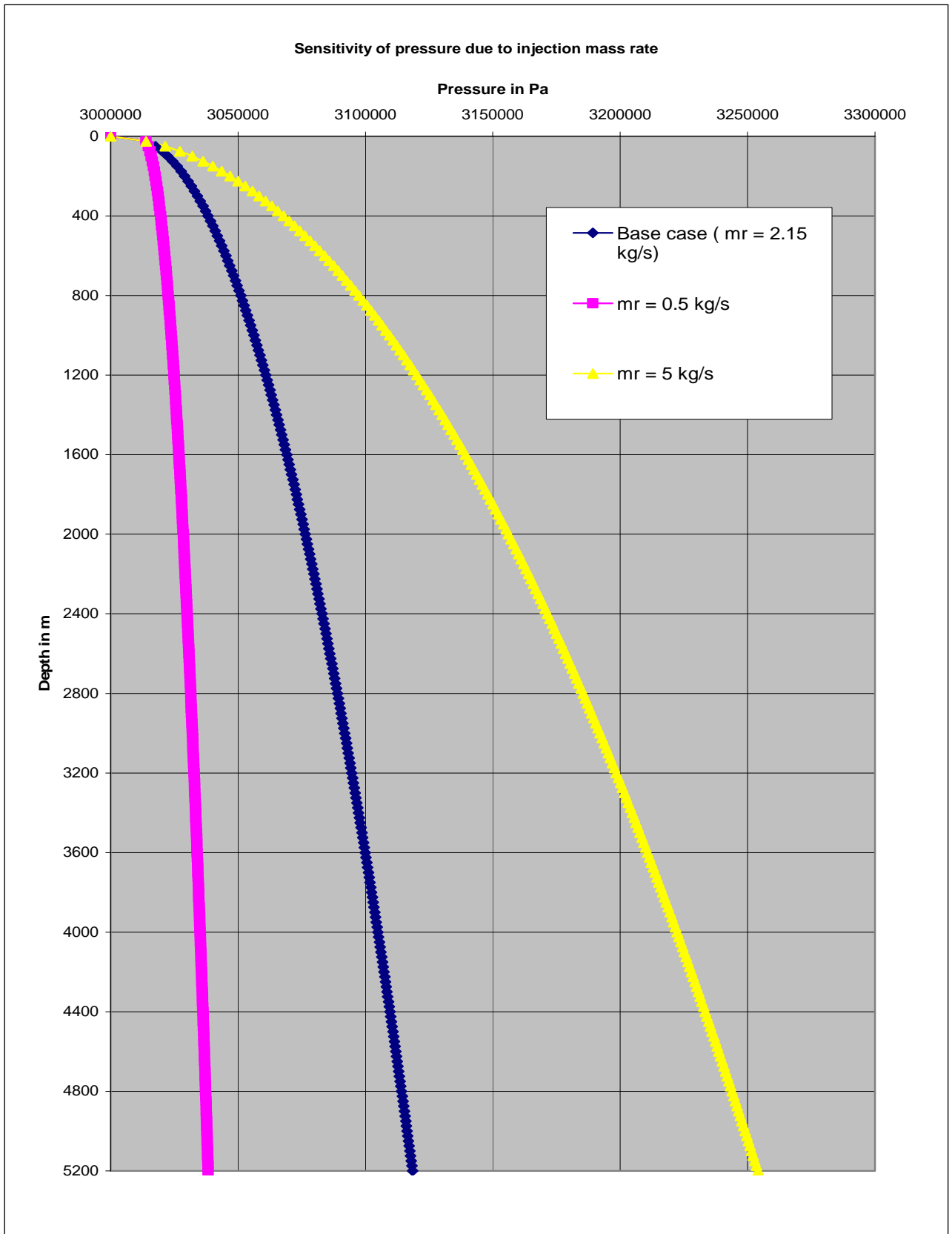


Fig.3.3.2.7 Sensitivity due to injection mass rate for isenthalpy flow

Table below is the summary for all the sensitivity analysis above which contains only the initial state and the end state of fluid flowing in the pipe.

Injection case	Pressure		Temperature	
	P_top	P_bottom	T_top	T_bottom
Base case	30	31.185	50	51.04
Pipe segment length = 12.5m	30	31.131	50	51.08
Pipe segment length = 50m	30	31.301	50	51.24
Pipe segment length = 100m	30	31.545	50	51.47
Temperature = 40 C	30	31.193	40	33.5
Temperature = 60 C	30	31.179	60	59.67
Temperature = 100 C	30	31.158	100	111.4
Top pressure = 20 bara	0*	1.129*	50	51.07
Top pressure = 40 bara	0*	1.245*	50	51.18
Top pressure = 100 bara	0*	1.1969*	50	51.08
Diameter = 4 inches	30	30.941	50	50.89
Diameter = 5 inches	30	30.653	50	50.62
Injection mass rate m = 0.5 kg/s	30	30.383	50	50.37
Injection mass rate m = 5 kg/s	30	32.541	50	52.4

Table 3.3.2 Summary of sensitivity analysis of steady state isenthalpy flow

The “star superscript” sign refers to normalized value (i.e. the pressure – the initial/top pressure). Unit of pressure is bara and unit of temperature is °C.

Some points from graphs above:

- The pressure changes rapidly in the beginning of the flow and then forms linear trend with the increase of the depth. It implies that the density drop very much in the beginning then latter toward a constant value of density.
- Temperature profile has the same shape with pressure profile. This is due to the Joule-Thomson coefficients in this particular injection area are positive value (i.e. the increase of pressure causes the increase of temperature and the decrease of pressure causes the decrease of temperature).
- The resolution of calculation plays important role to determine the accuracy of pressure profile calculation. However, because the change of pressure between

top and bottom pressure is small, actually in larger scale of pressure, the different is insignificant. The different in graph looks large because the “zoom effect”. The large different in pressure at each depth is because we calculate the pressure in the next segment using hydrostatic approach which is sensitive to the length of pipe segment. The graph shows that an overestimate in the pressure profile calculation if using the large length of pipe segment.

- In the calculation, specific volume of the next segment is determined by the specific volume of the segment and other term which proportional to ratio between cross sectional area and mass rate. The increase of initial temperature causes the increase of specific volume which means the decrease of initial density. Thus, the pressure is decreased. We observe that the pressure profile for high surface injection temperature is lower than the low surface injection temperature.
- The increment of bottom pressure due to the increase of top pressure is not linear as well as in the previous scenario.
- Pipe diameter size gives the influences to specific volume by the merit of cross section area. The larger cross section area, the larger specific volume is. Afterward, the density is smaller. So does the pressure. So, larger pipe diameter gives the lower pressure profile.
- Mass rate injection is reverse proportional to specific volume. The larger the mass rate injection, the smaller the specific volume is. It causes the density to increase and pressure as well. The pressure profile for higher mass injection rate would be above for lower mass injection rate.

3.3.3 Steady State Unisenthalpy flow – friction approach

The base case for this scenario is

Surface injection temperature: 50 °C

Surface injection pressure: 30 bara

The length of vertical pipe: 5200 meters

Diameter of pipe: 3.5 inches

Mass rate injection: 2.15 kg/s

Dimensionless roughness of pipe: 0.0005

Pressure and temperature distribution are calculated based on pipe segment length of 100 m and using PR-EOS.

Sensitivity analysis (pressure and temperature):

- Pipe segment length: 25 m
- Surface injection temperature: 40 °C, 60 °C, 100 °C
- Surface injection pressure: 20 bara, 40 bara, 100 bara
- Pipe diameter: 4 inches, 5 inches
- Injection mass rate: 0.5 kg/s, 5 kg/s
- Dimensionless roughness : 0, 0.01

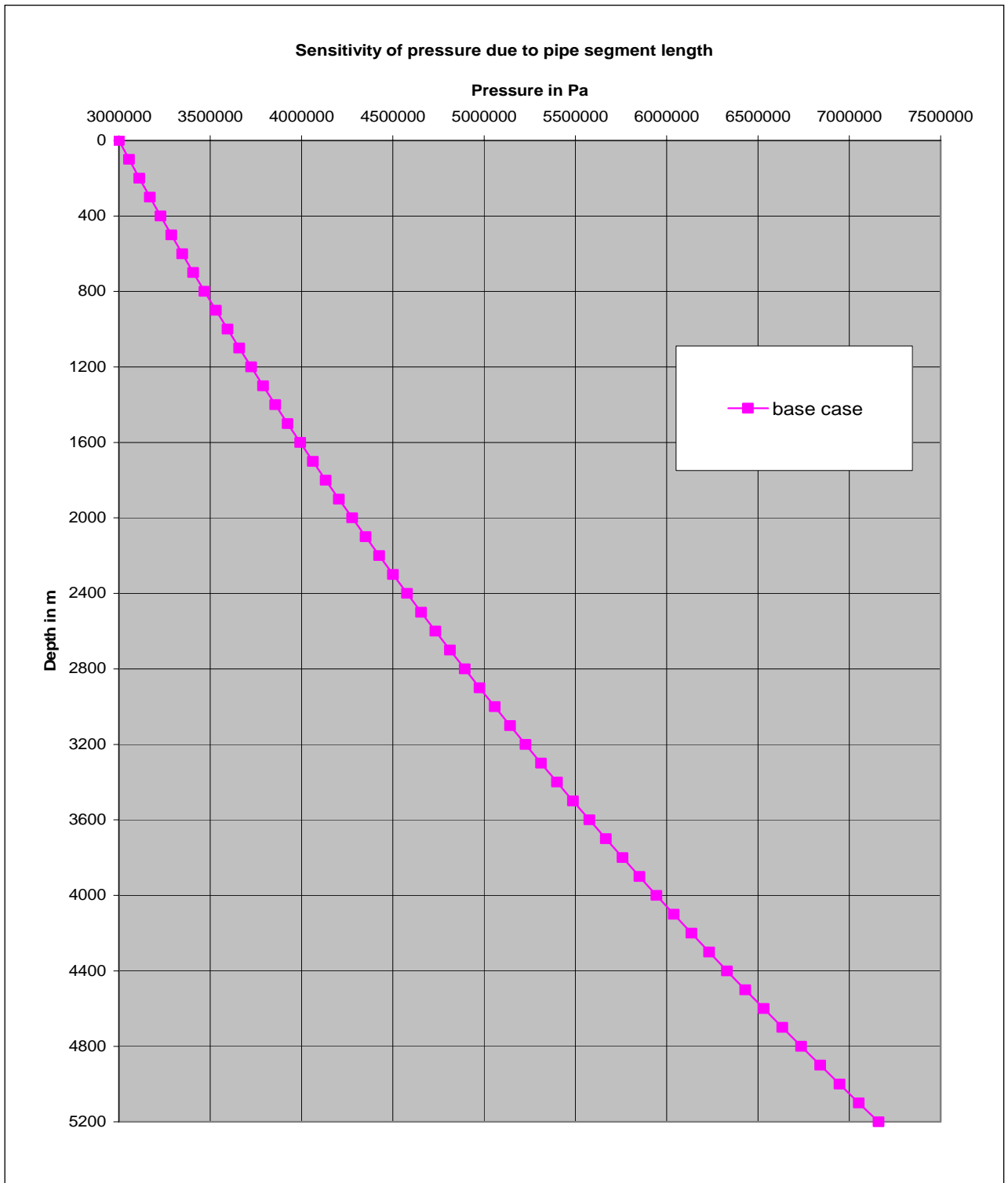


Fig. 3.3.3.1 Pressure profile of base case of steady state unisenthalpy flow-friction approach

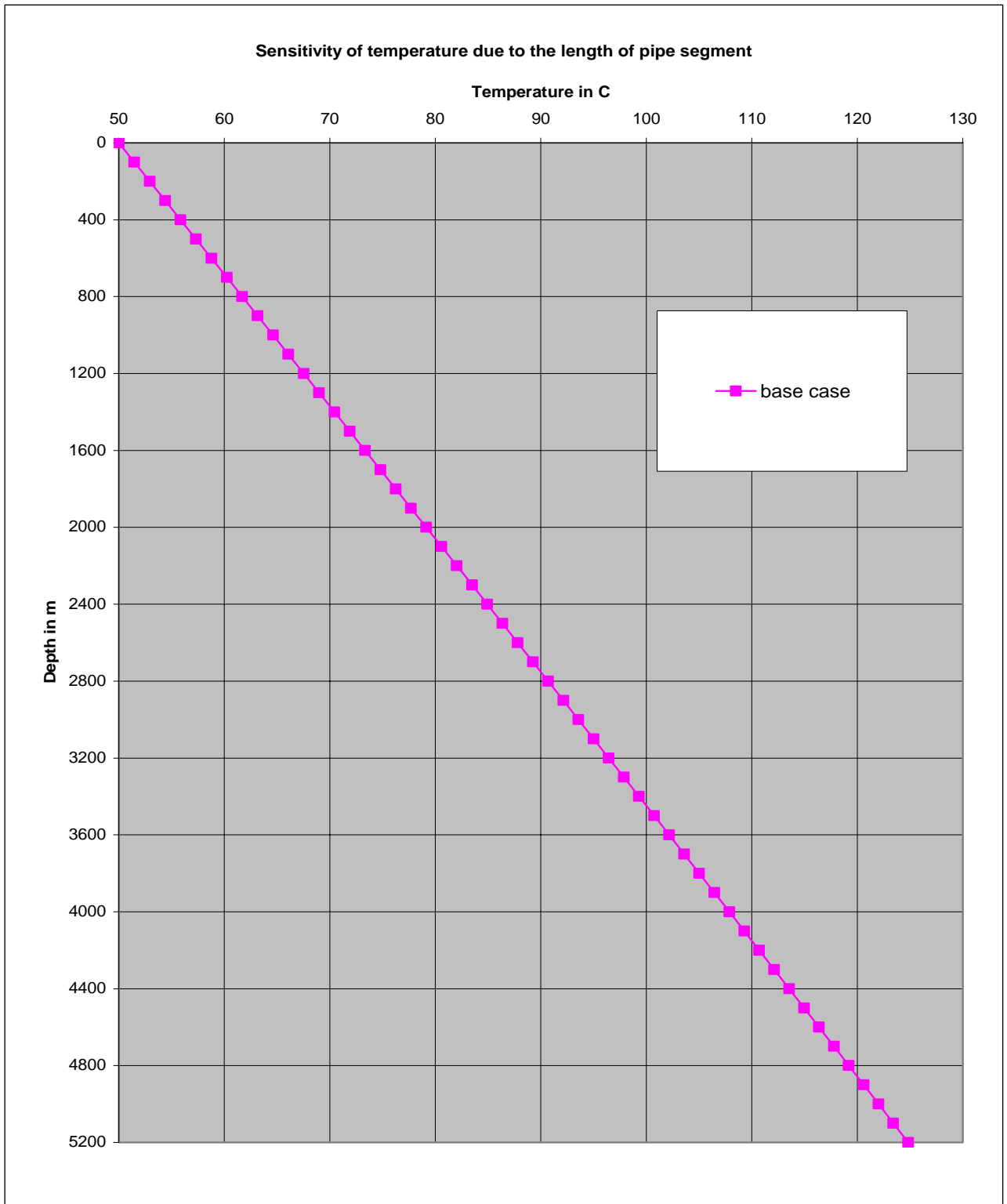


Fig. 3.3.3.2 Temperature profile of base case of steady state unisenthalpy flow-friction approach

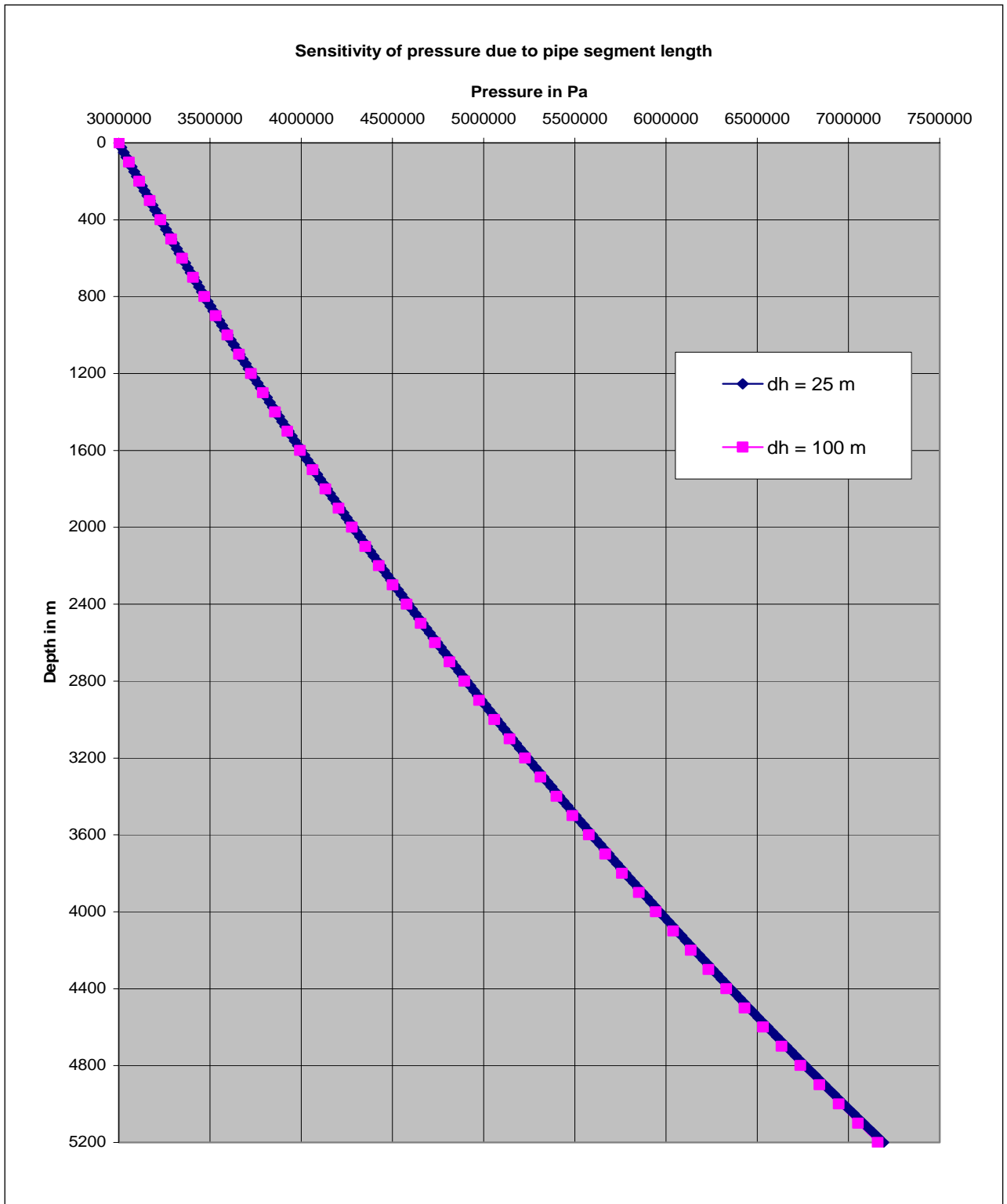


Fig. 3.3.3.3 Pressure sensitivity due to the length of pipe segment for unisenthalpy flow-friction approach

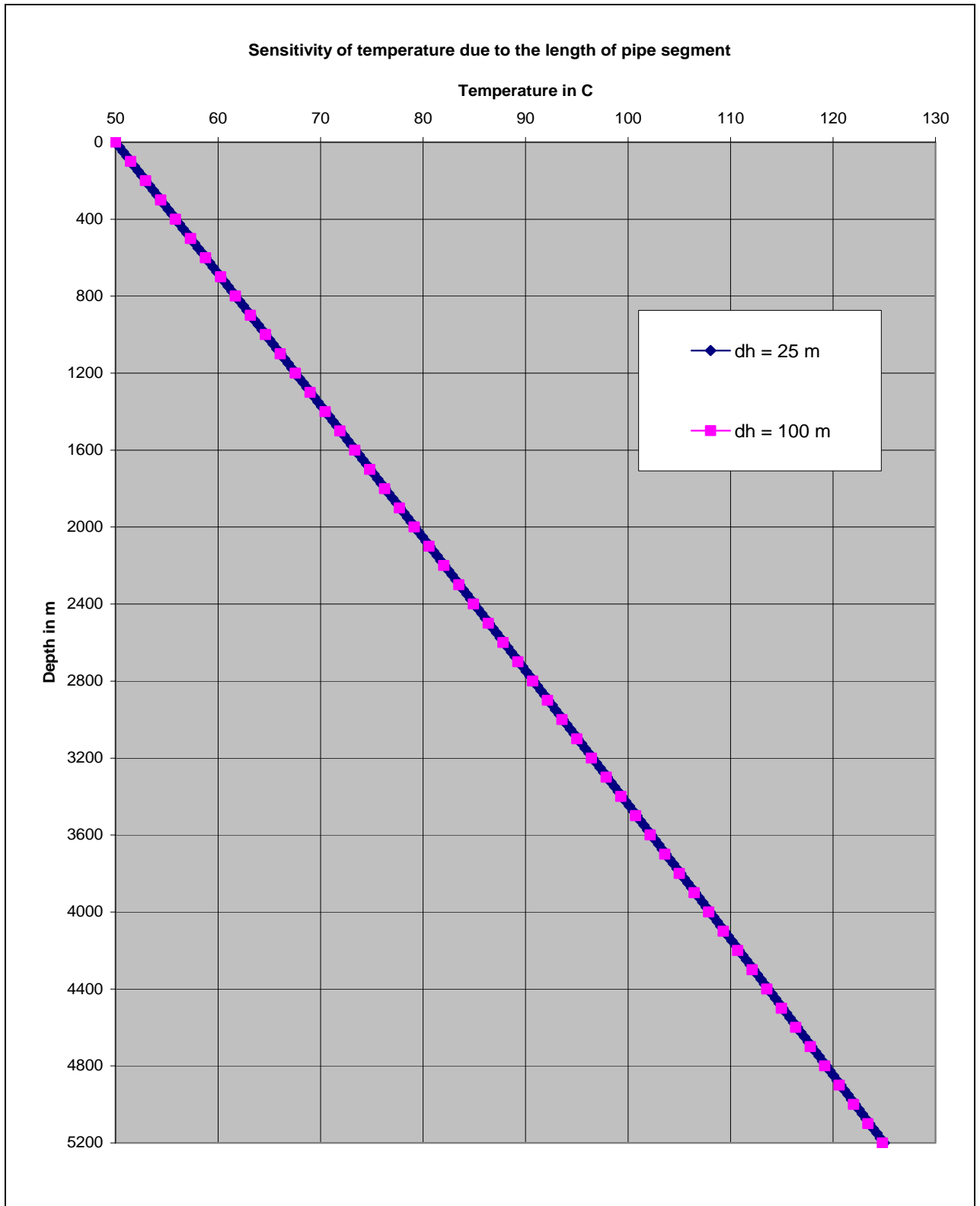


Fig. 3.3.3.4 Temperature sensitivity due to the length of pipe segment for unisenthalpy flow-friction approach

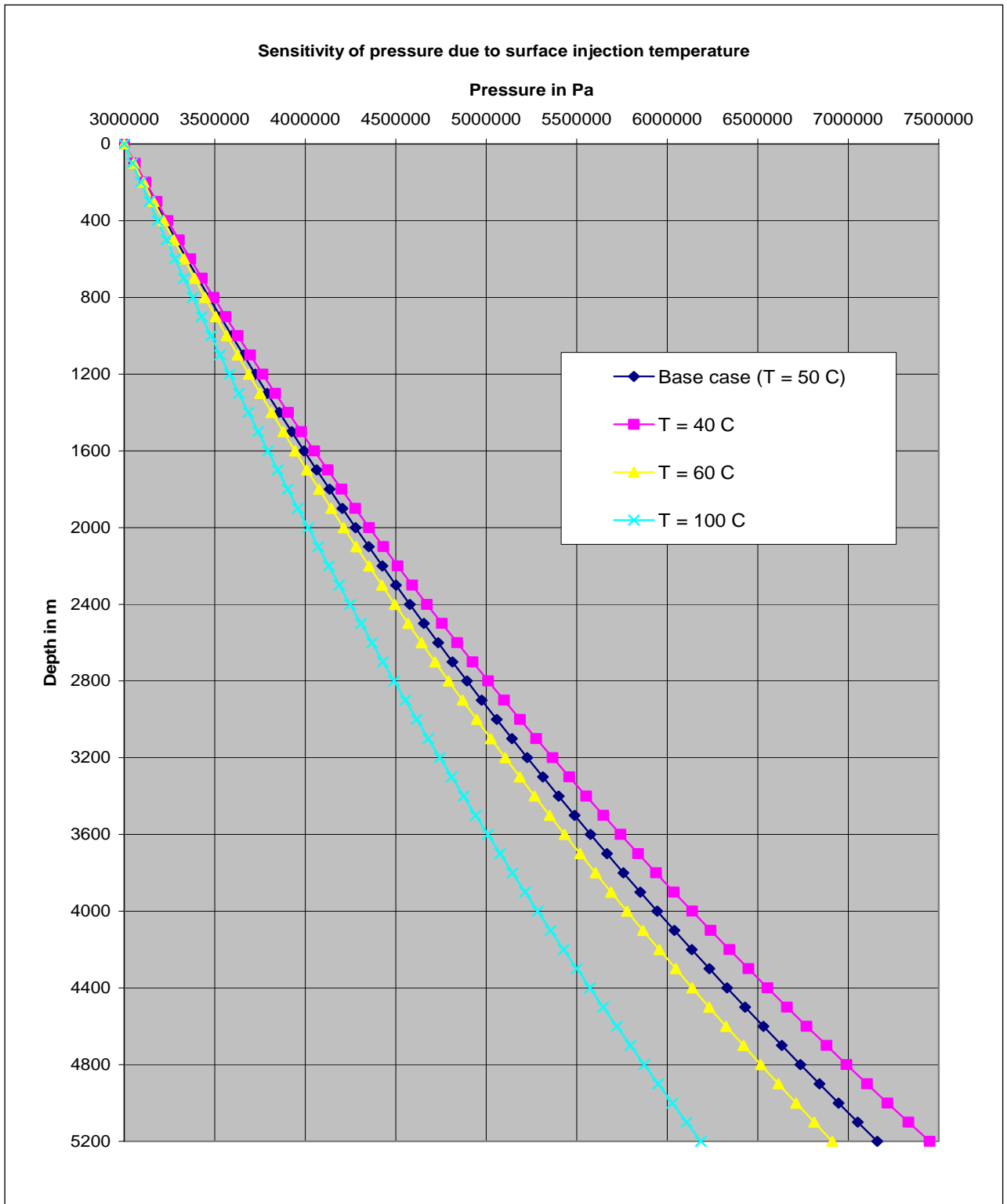


Fig. 3.3.3.5 Pressure sensitivity due to the surface injection temperature for unisenthalpy flow-friction approach

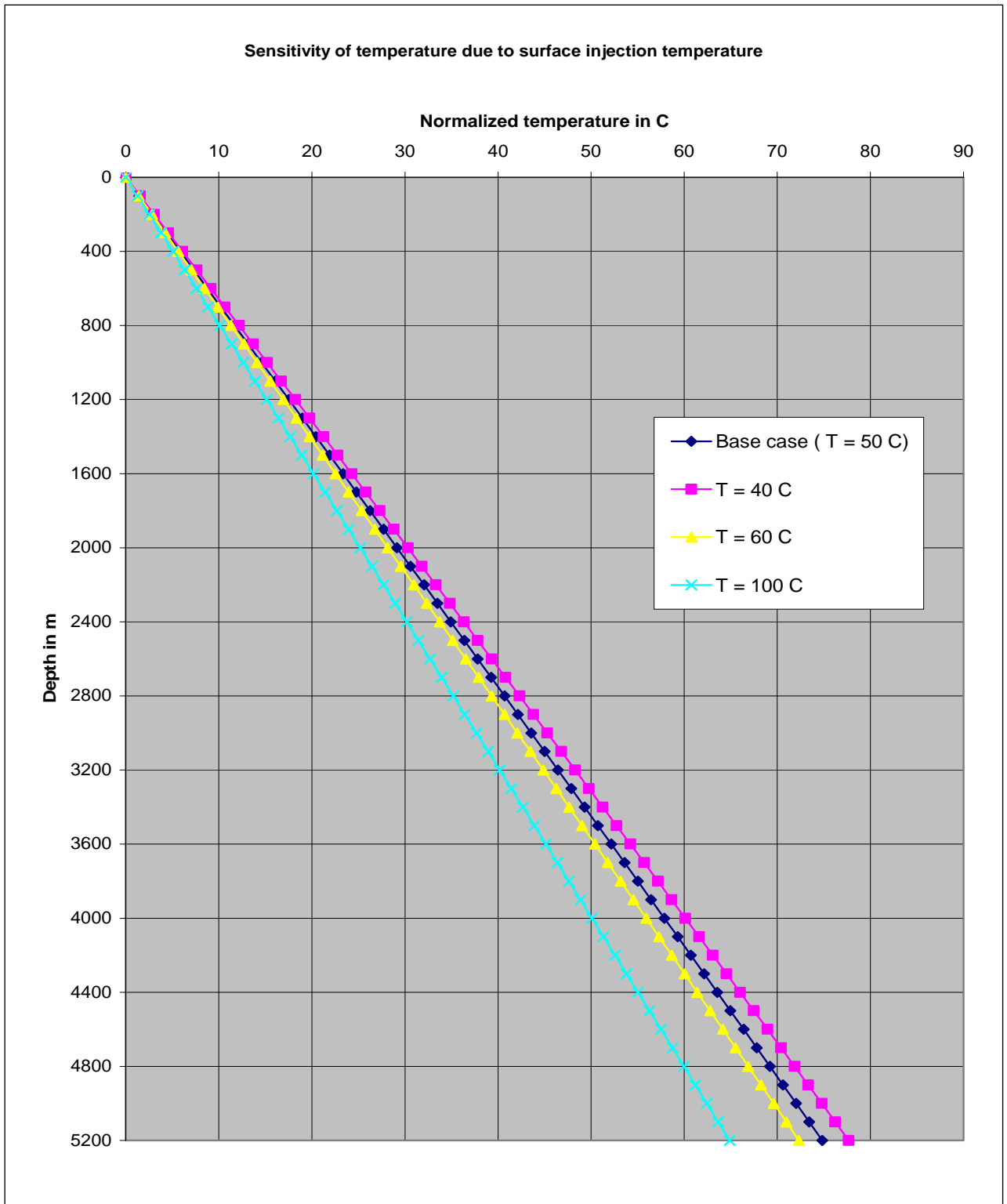


Fig. 3.3.3.6 Temperature sensitivity due to the surface injection temperature for unisenthalpy flow-friction approach

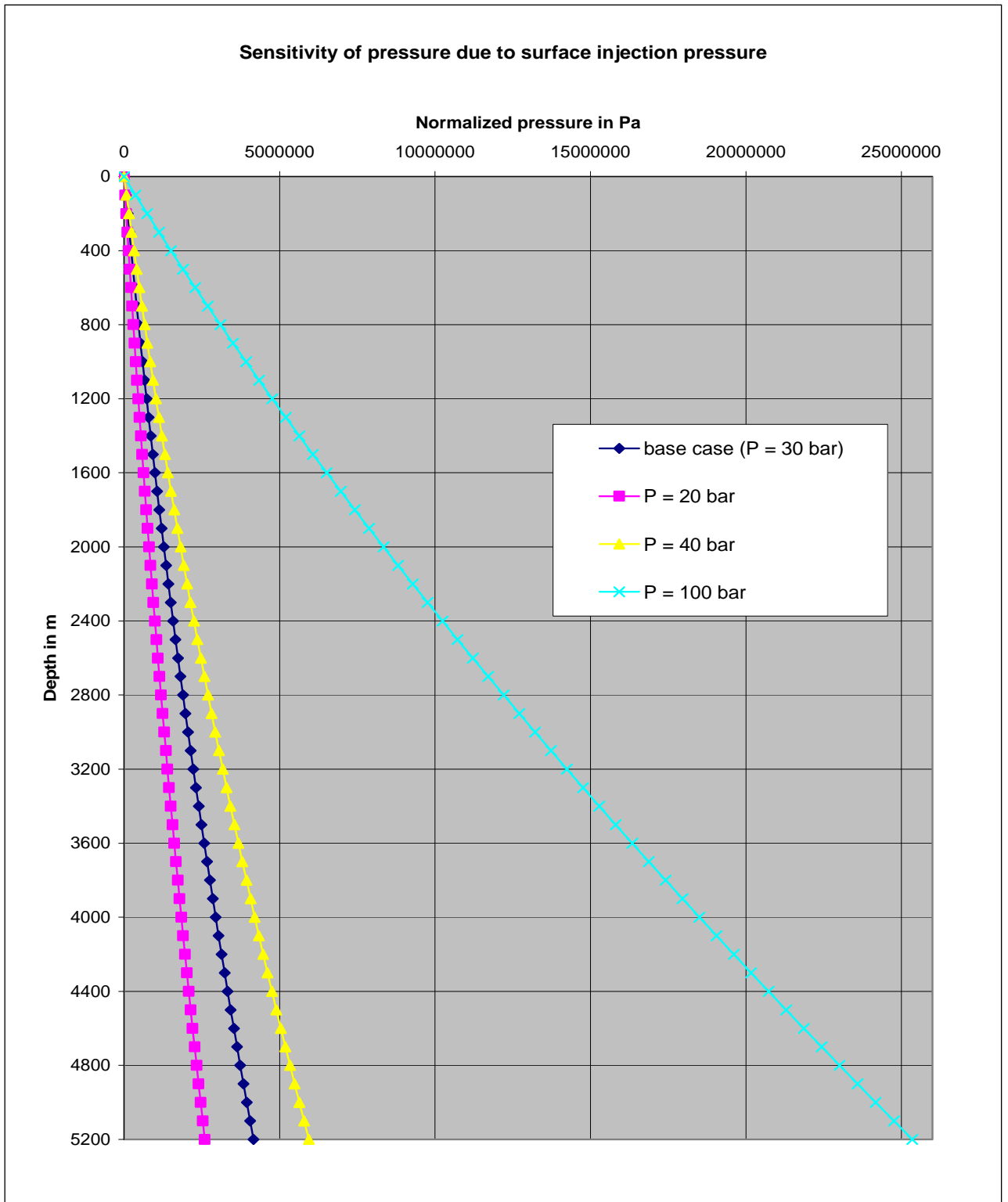


Fig. 3.3.3.7 Pressure sensitivity due to the surface injection pressure for unisenthalpy flow-friction approach

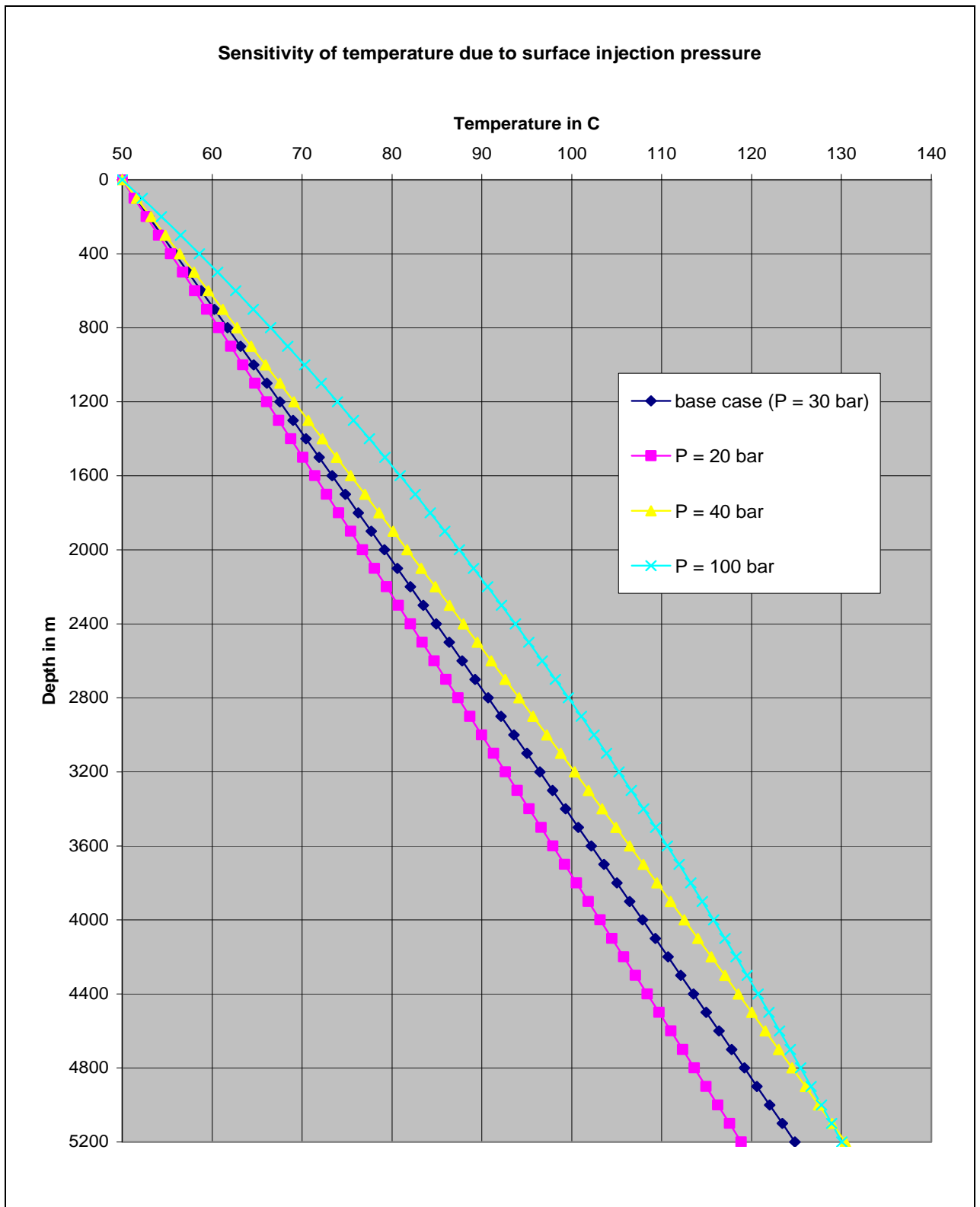


Fig. 3.3.3.8 Temperature sensitivity due to the surface injection pressure for unisenthalpy flow-friction approach

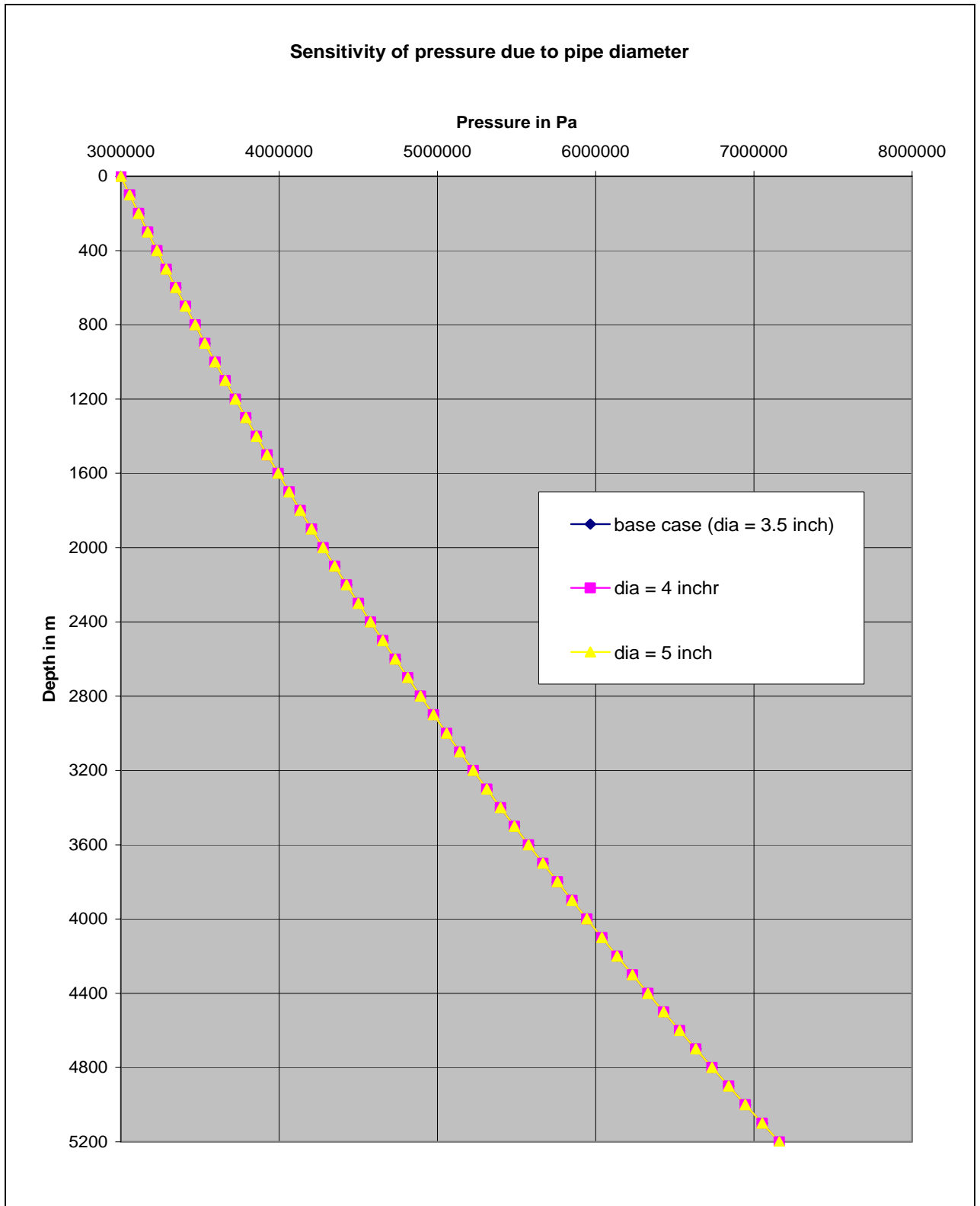


Fig. 3.3.3.9 Pressure sensitivity due to the size of pipe diameter for unisenthalpy flow-friction approach

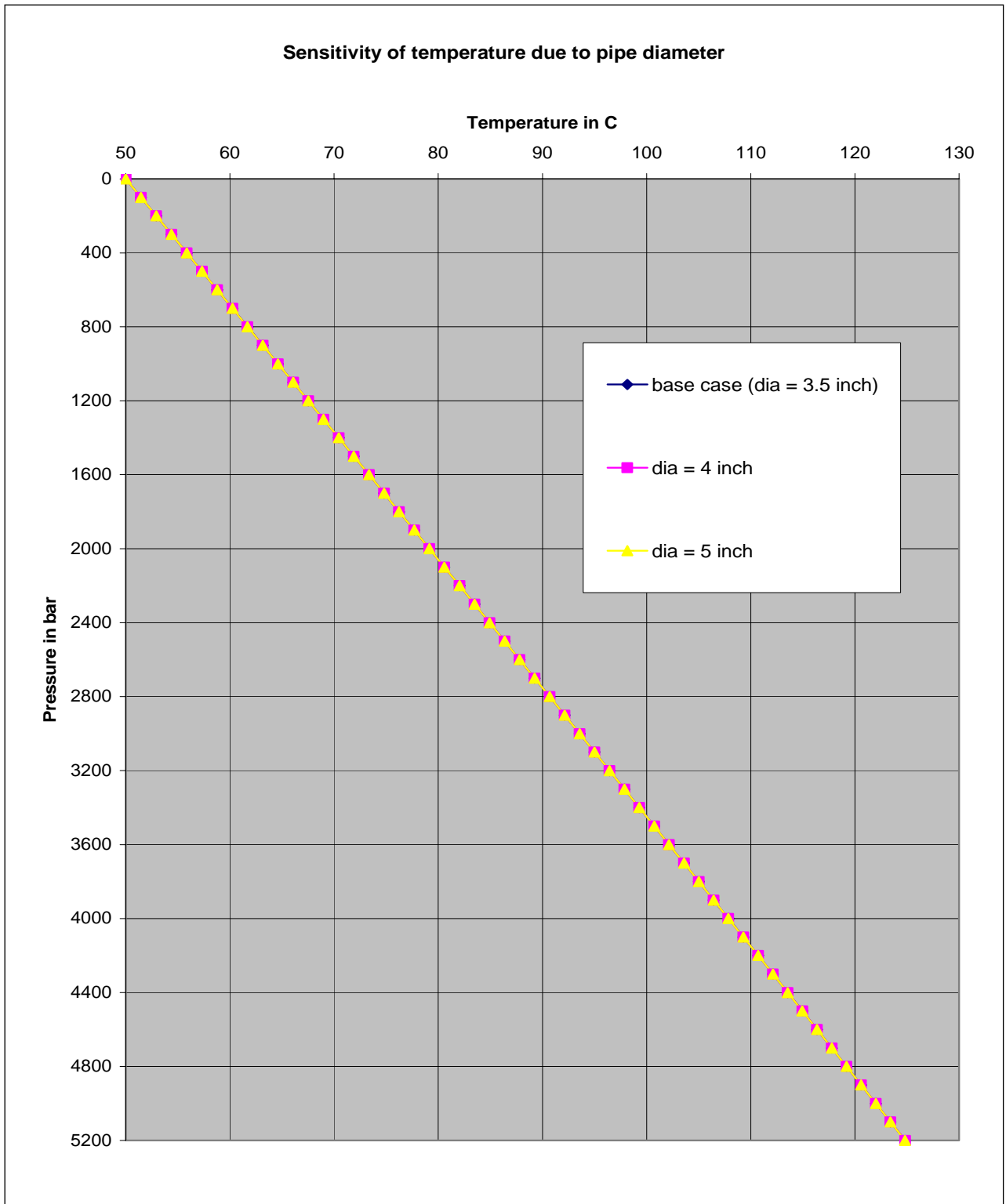


Fig. 3.3.3.10 Temperature sensitivity due to the size of pipe diameter for unisenthalpy flow-friction approach

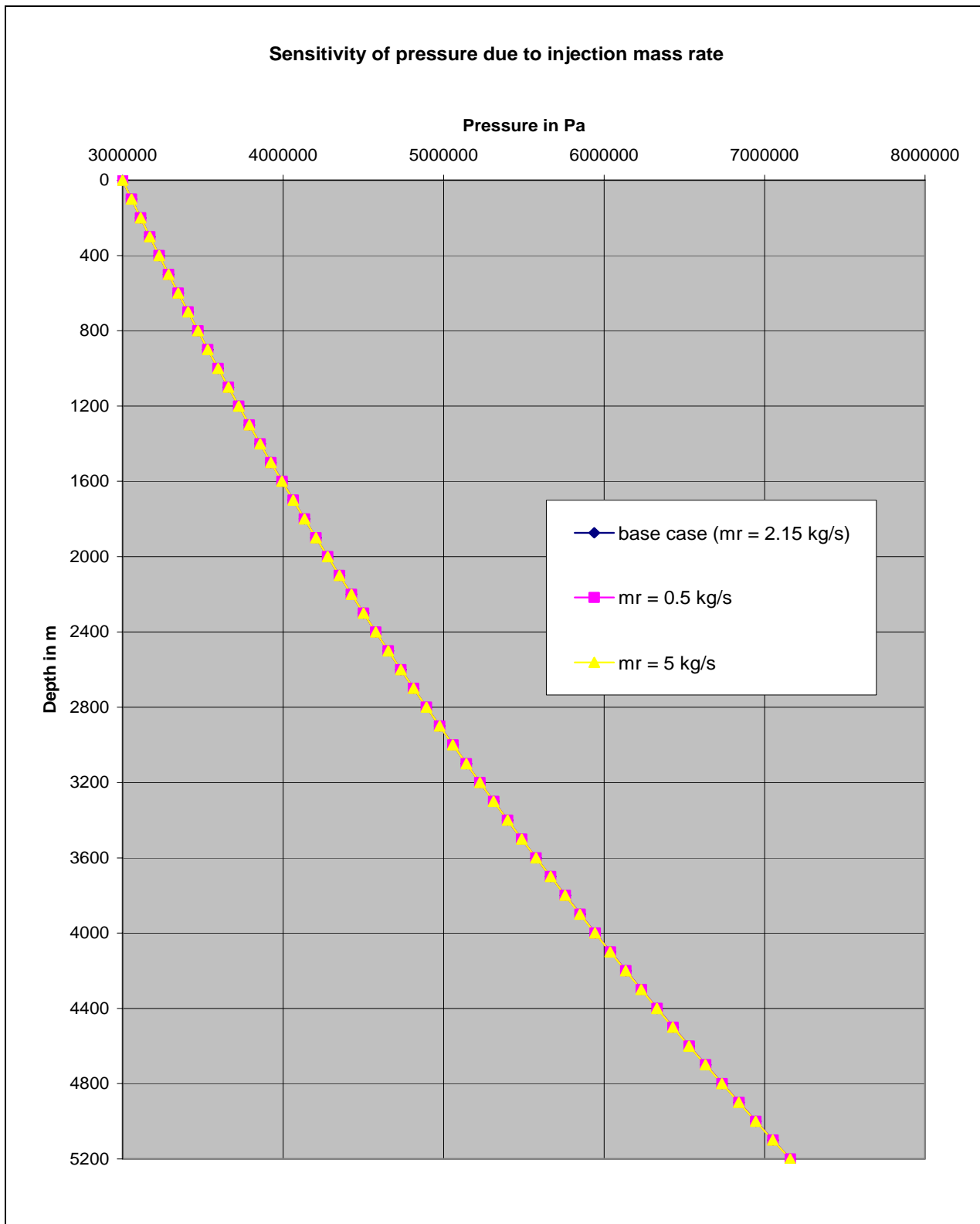


Fig. 3.3.3.11 Pressure sensitivity due to the injection mass rate for unisenthalpy flow-friction approach

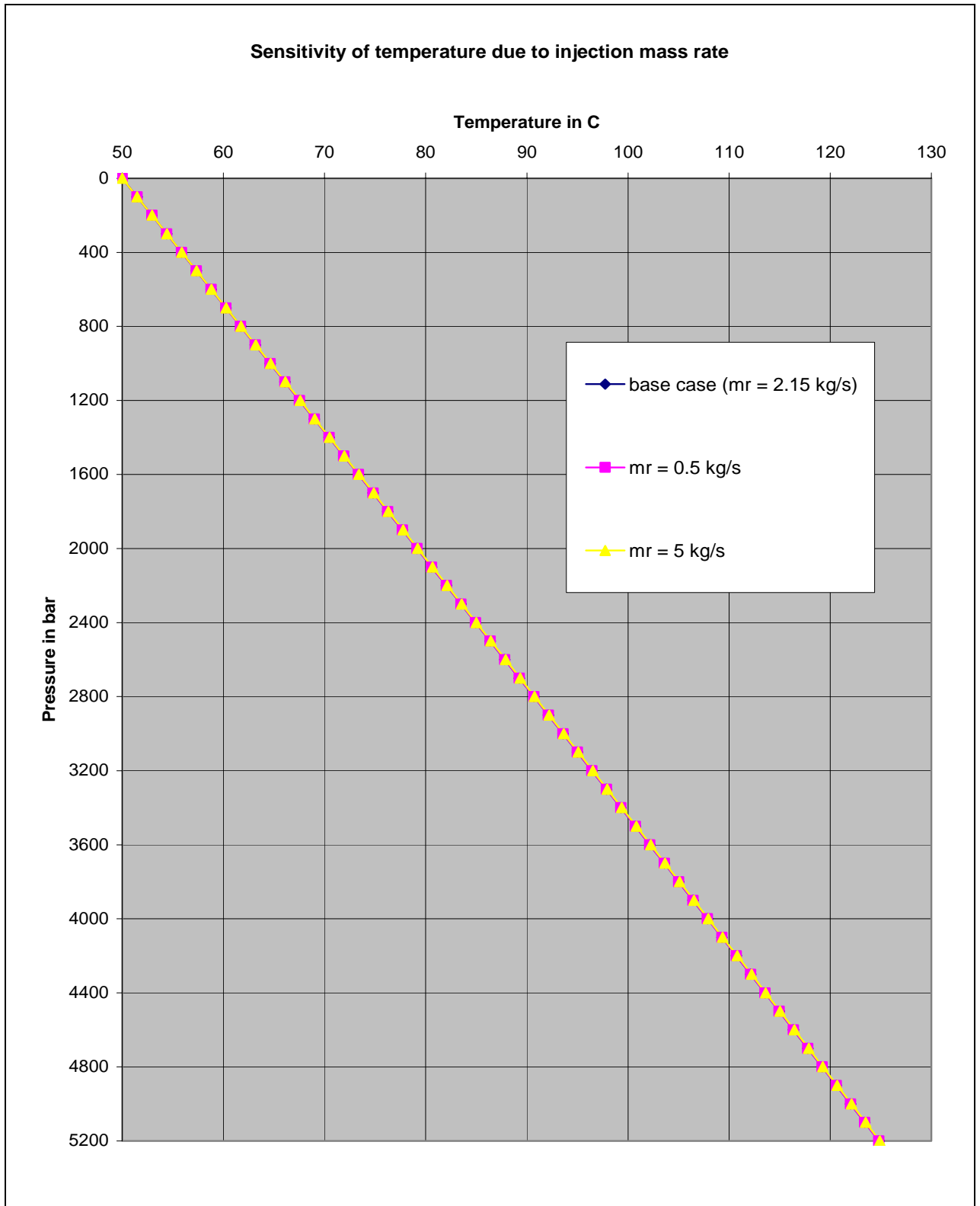


Fig. 3.3.3.12 Temperature sensitivity due to the injection mass rate for unisenthalpy flow-friction approach

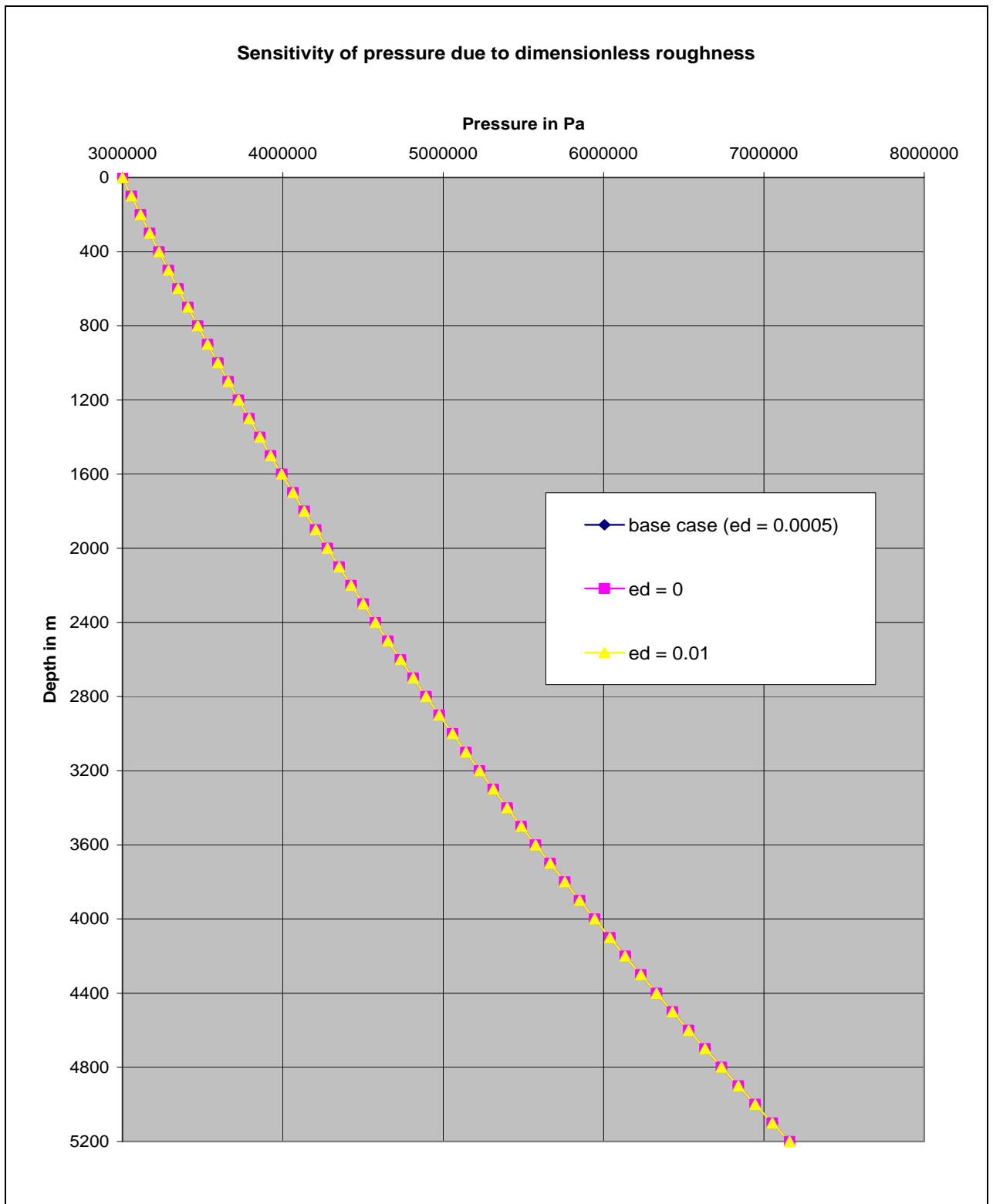


Fig. 3.3.3.13 Pressure sensitivity due to the dimensionless roughness for unisenthalpy flow-friction approach

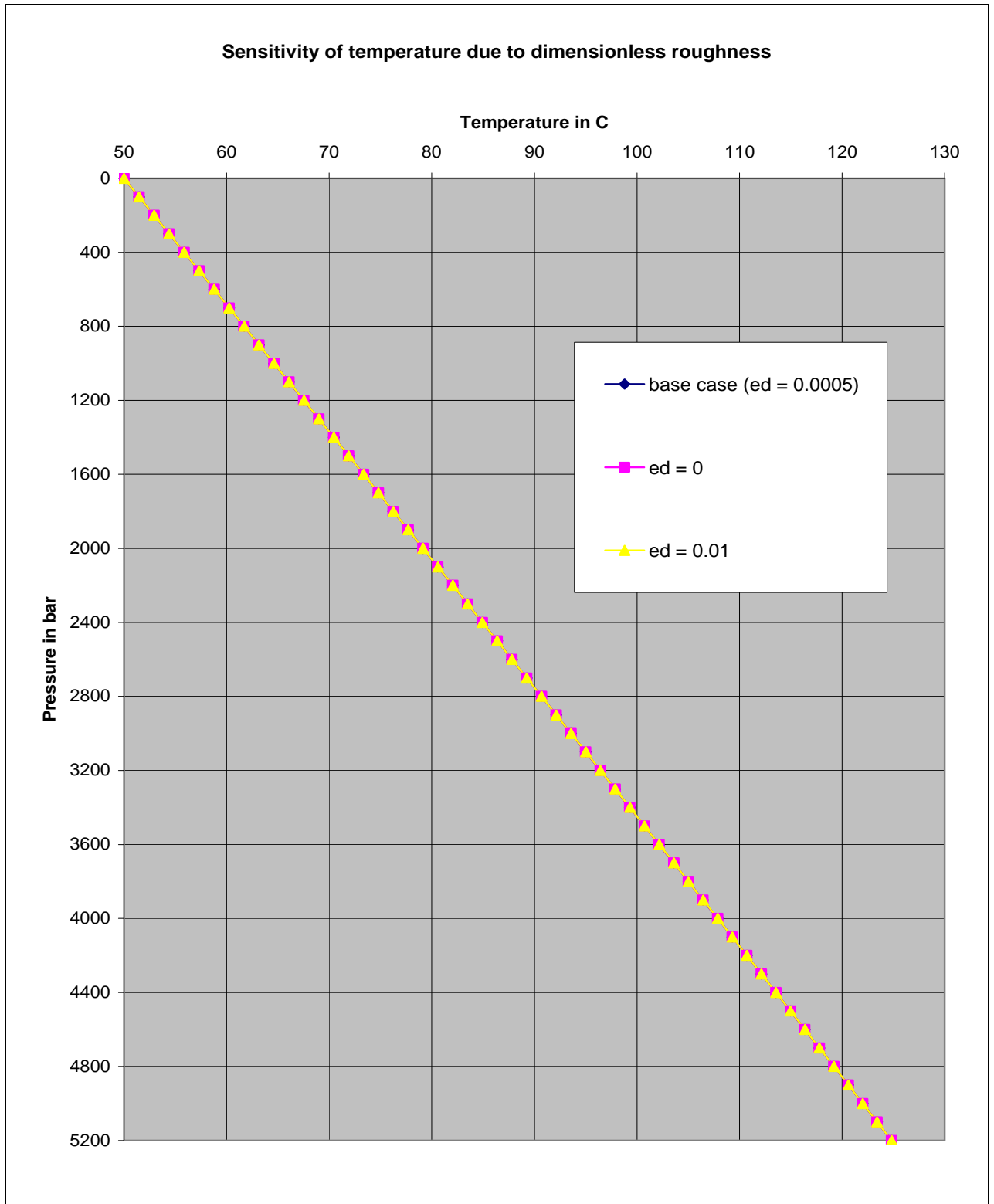


Fig. 3.3.3.14 Temperature sensitivity due to the dimensionless roughness for unisenthalpy flow-friction approach

All the sensitivity analysis above can be summarized in the table below which contains only the surface injection state and bottom pipe state:

Injection case	Pressure		Temperature	
	P_top	P_bottom	T_top	T_bottom
Base case	30	71.6068	50	124.82
Pipe segment length = 25m	30	71.912	50	124.984
Temperature = 40 C	30	74.498	0*	77.675*
Temperature = 60 C	30	69.124	0*	72.332*
Temperature = 100 C	30	61.853	0*	64.871*
Top pressure = 20 bara	0*	25.966*	50	118.85
Top pressure = 40 bara	0*	59.451*	50	130.432
Top pressure = 100 bara	0*	253,504*	50	130.03
Diameter = 4 inches	30	71.6072	50	124.819
Diameter = 5 inches	30	71.6074	50	124.818
Injection mass rate m = 0.5 kg/s	30	71.6074	50	124.818
Injection mass rate m = 5 kg/s	30	71.6059	50	124.906
Dimensionless roughness ed = 0	30	71.607	50	124.819
Dimensionless roughness ed = 0.01	30	71.6059	50	124.825

Table 3.3.3 Summary of sensitivity analysis of steady state unisenthalpy flow- friction approach

The “star superscript” sign refers to normalized value (i.e. the pressure/temperature – the initial/top pressure/temperature). Unit of pressure is bara and unit of temperature is °C.

Some points from the graphs above:

- For this particular case, the pressure profile trend is not linear while the temperature profile is linear.
- The pipe segment length doesn’t give the significant change of bottom pipe pressure. It will slightly larger for shorter pipe segment length. For temperature, it is practically the same for the larger or the shorter one. Our calculation is based on 100 meters pipe segment length. This is due the “time saving” when we run the program. For example: for one case and based on 100 meter calculation, the time

needed by MATLAB is about 25 minutes and when we changed to 25 meter calculation the time yields until more than 1 hour. However, due to only slightly change on bottom pressure due to pipe segment length, we can assume that 100 meter calculation represents the “true” value (i.e. the segment length is equal to zero) of pressure and temperature.

- The transfer of the potential energy changes to fluid temperature and pressure is the main key to understand the behavior of pressure and temperature profile in connection with injection parameters. In this scenario, we assume the internal energy change is due to friction only. Internal energy itself is the function of pressure and temperature. For injection case, the pressure is increased when the depth increases. Assumption of adiabatic system implies that no energy is given and/or withdrawn to/from surroundings, lead to the increase in fluid particles kinetic energy due to change of macroscopic fluid potential energy. It increases the temperature of fluid which latter increases the pressure of the fluid. Finally it increases the enthalpy which indeed causing the pressure and temperature to increase. In other words, the potential energy changes in this scene are given to increase the fluid temperature then to fluid pressure.
- Higher injection temperature will lead to lower enthalpy changes that cause the lower temperature changes. It doesn't necessarily cause the pressure to be lower but in this case it does. It is as seen in the graphs that higher injection temperature case will have pressure and temperature profile lower than lower injection temperature case.
- The mechanism of injection pressure case is reversal with the injection temperature case. Higher injection pressure leads to higher enthalpy changes. Thus, higher temperature and then higher pressure. The graphs show agreement with this explanation. It has to be notice that at high pressure injection, the temperature profile is not longer linear but forms the arc shape where the temperature at the bottom tends to decrease.
- For larger size of pipe diameter the friction force will be less. It also causes the enthalpy to be less. The effect of this is temperature also to be less but not necessarily for pressure. We observe that the increase of pressure occur rather

than the decrease of pressure. The reason for this will be explained on the next subchapter. However, the changes are insignificant in this particular sensitivity analysis.

- High injection mass rate causes the high fluid velocity. Thus, the friction will be high as well and this gives the high enthalpy changes. It causes the temperature to be higher but not necessarily for pressure. We observe that for higher injection rate case, the end temperature is higher than the lower injection rate case but reversal way for the bottom pressure
- The smooth pipe gives almost no friction to the fluid flow. The contribution of friction to the changes of enthalpy also almost nothing. This gives effect to lowering the temperature but again, not necessarily for pressure. Observation shows the same pattern as for the size of pipe diameter and mass injection rate.

3.3.4 Steady State Unisenthalpy flow – Constant Internal Energy

The base case for this scenario is

Surface injection temperature: 50 °C

Surface injection pressure: 30 bara

The length of vertical pipe: 5200 meters

Diameter of pipe: 3.5 inches

Mass rate injection: 2.15 kg/s

Dimensionless roughness of pipe: 0.0005

Pressure and temperature distribution are calculated based on pipe segment length of 25 meter and using PR-EOS.

We don't do the sensitivity analysis for this scenario. We just compare the result from this scenario with the scenario of Steady state flow-friction approach. The purpose of doing this is to observe how would the contribution of the change of internal energy and the effect of it to the pressure and temperature profile calculation.

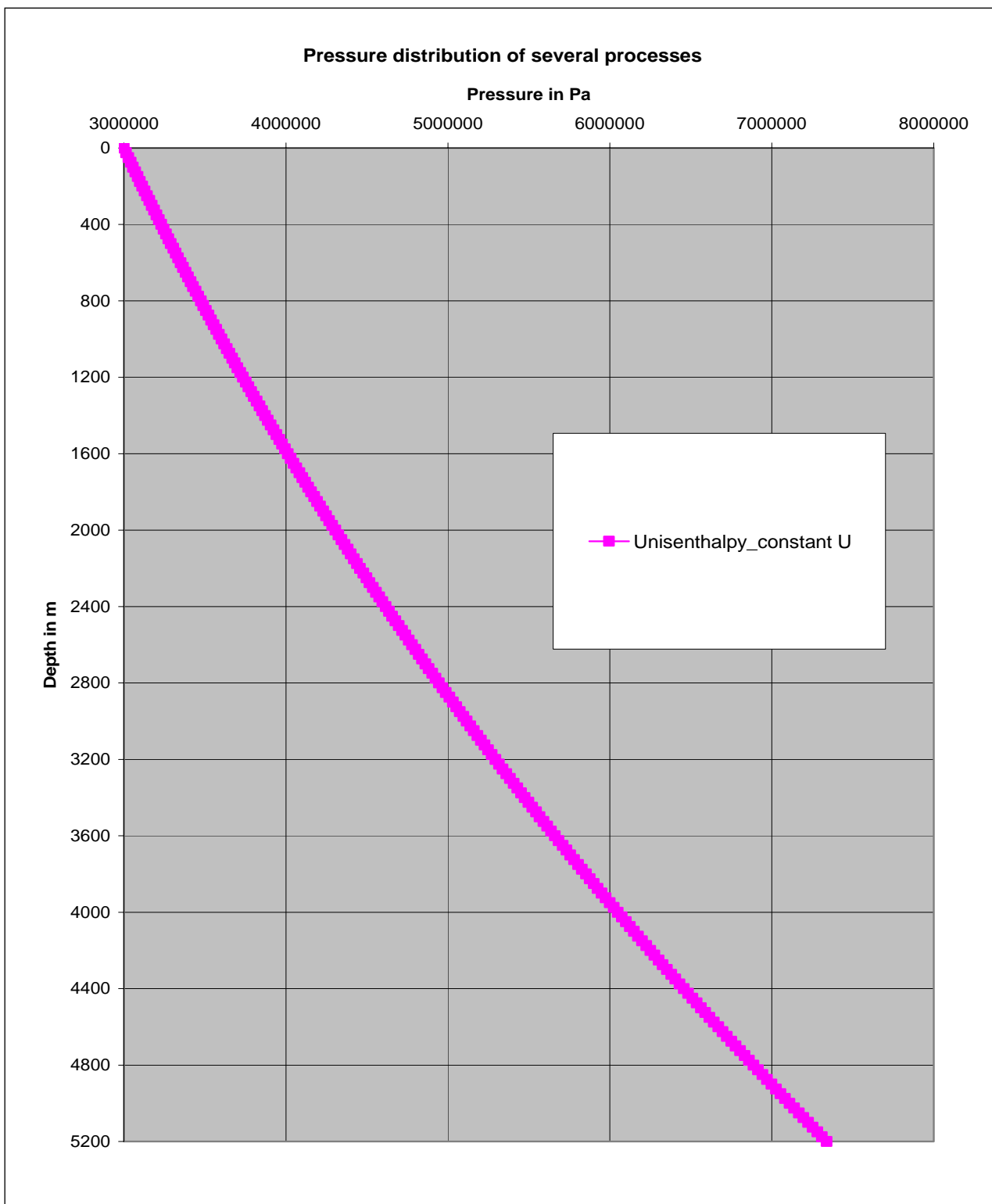


Fig. 3.3.4.1 Pressure profile of base case of steady state unisenthalpy flow-constant internal energy approach

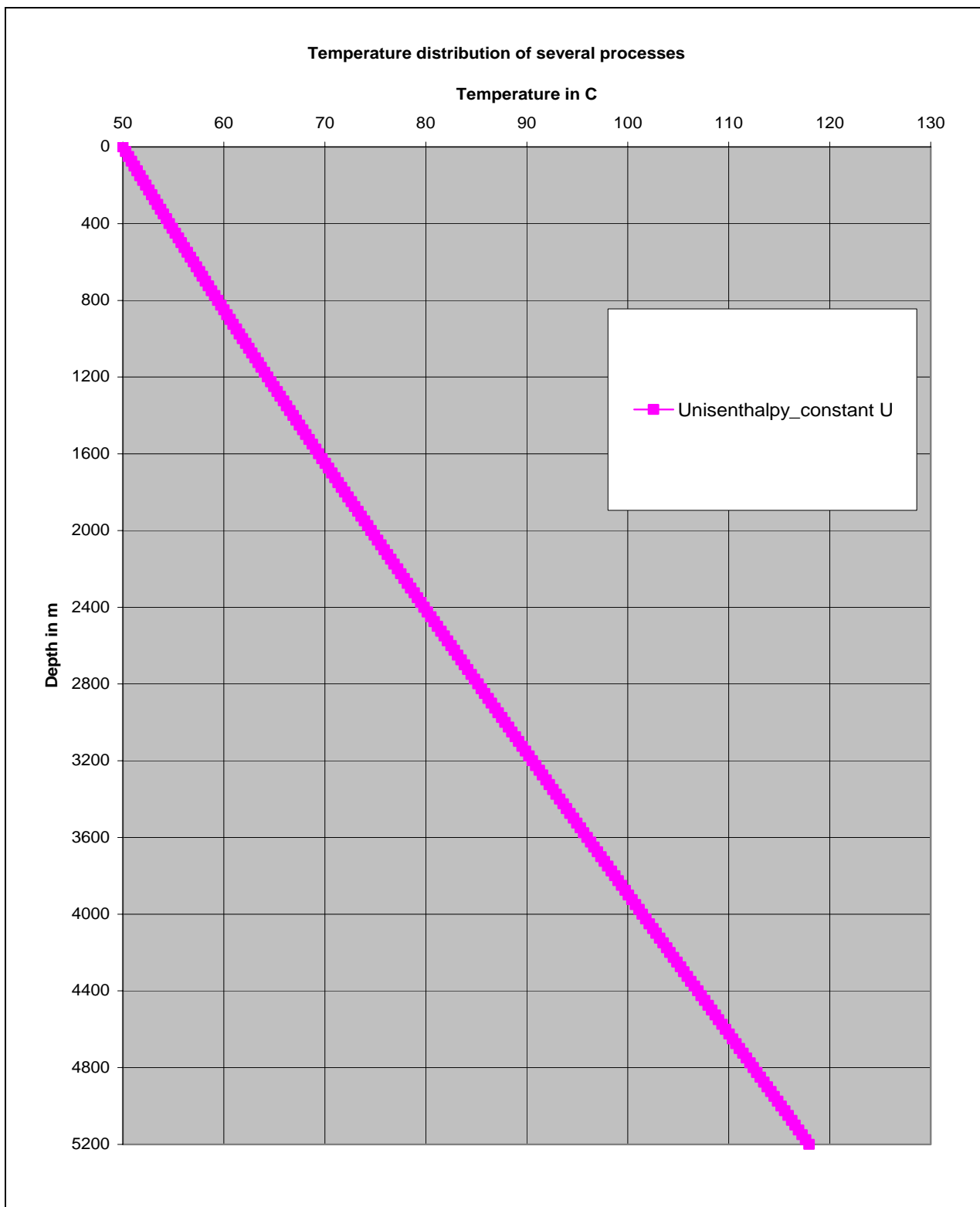


Fig. 3.3.4.2 Temperature profile of base case of steady state unisenthalpy flow-constant internal energy approach

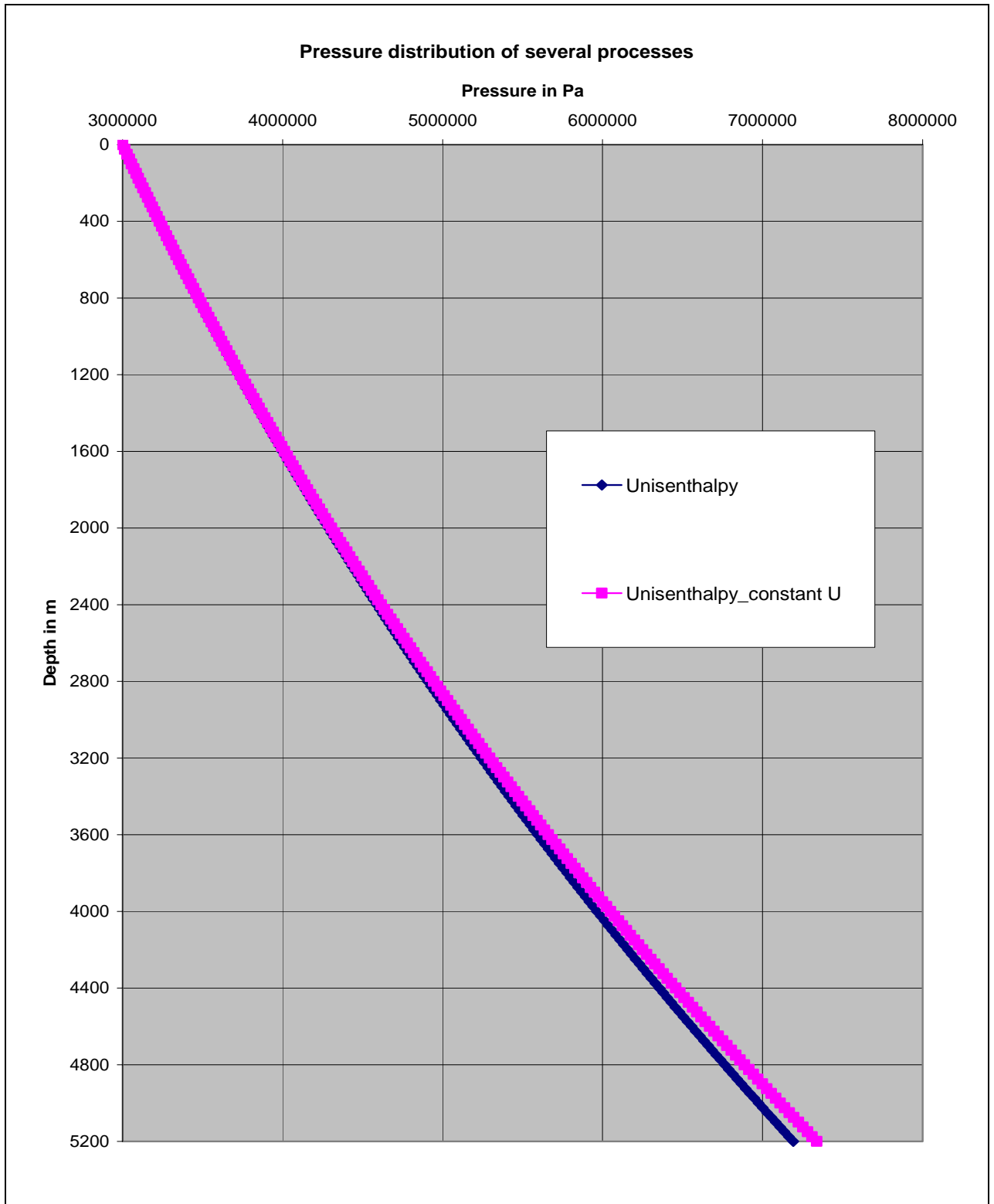


Fig. 3.3.4.3 Pressure profile comparison of base case between steady state unisenthalpy flow-friction and constant internal energy approaches

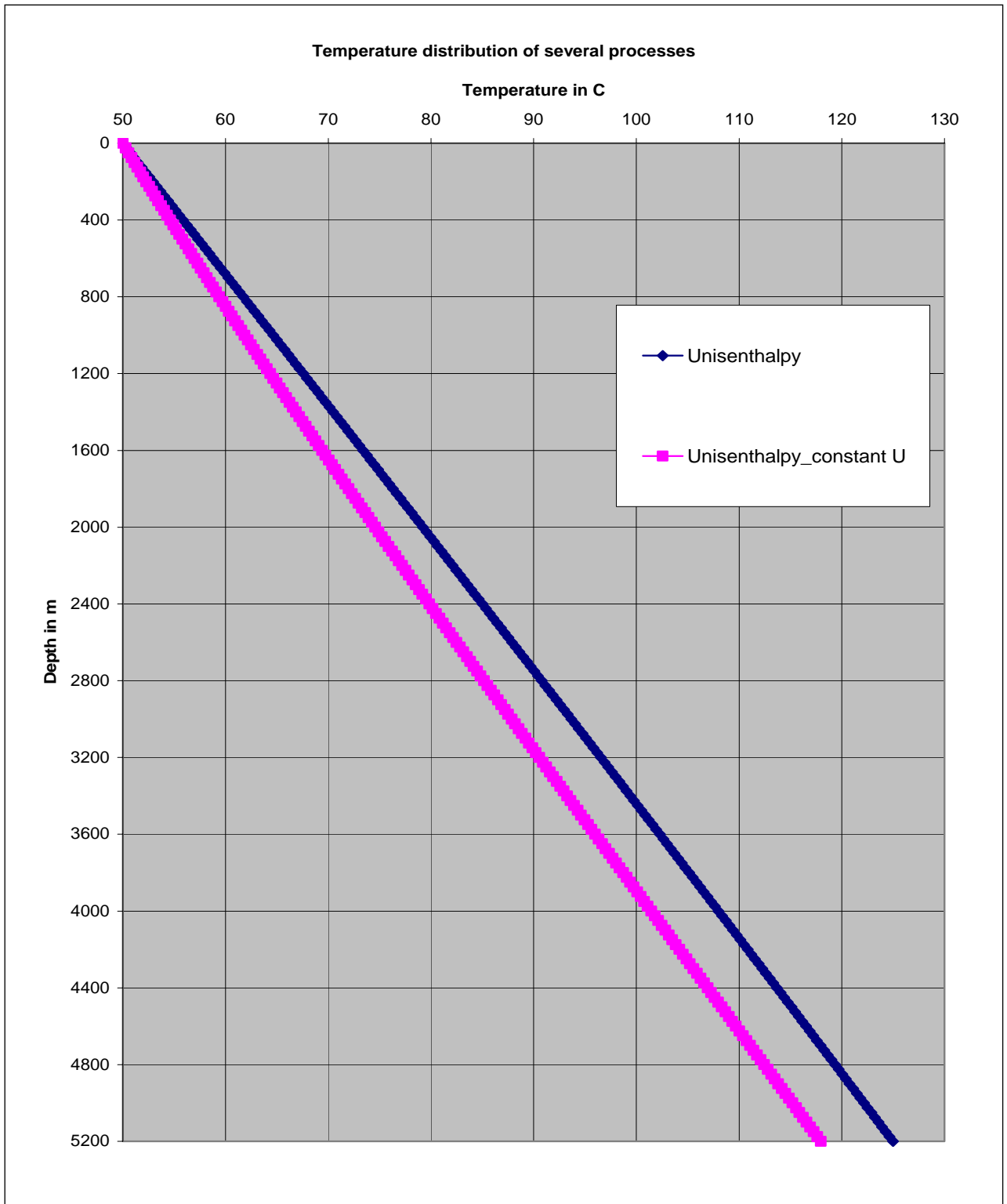


Fig. 3.3.4.4 Temperature profile comparison of base case between steady state unisenthalpy flow-friction and constant internal energy approaches

The graphs above can be summarized in the table below:

Injection case	Pressure		Temperature	
	P_top	P_bottom	T_top	T_bottom
Unisenthalpy-friction approach	30	71.912	50	124.984
Unisenthalpy-constant Int. Energy	30	73.386	50	117.957

Table 3.3.4 Comparison between Unisenthalpy-friction approach and Constant Internal Energy approach

Unit of pressure is bara and unit of temperature is °C.

The difference between both is in the internal energy different term in energy balance equation. The friction approach assumes that internal energy changes can be approximated by the energy dissipated due to friction while the constant internal energy method assumes this value equal to zero.

The enthalpy changes can be re-written as:

$$\Delta h = (u_2 - u_1) + \frac{P_2}{\rho_2} - \frac{P_1}{\rho_1}$$

or

$$P_2 = \rho_2 \left(\Delta h - (u_2 - u_1) + \frac{P_1}{\rho_1} \right)$$

From above equation, it is obvious that the friction approach has enthalpy changes larger than constant internal energy approach due to the contribution of internal energy difference. This larger change of enthalpy will lead to larger temperature at the bottom of pipe. Thus the bottom density will be reduced more for friction approach than constant internal energy approach.

Now assume that we have the same starting state, so $\frac{P_1}{\rho_1}$ has the same value for two approaches above. Now if we assume the difference of enthalpy changes is only due to

internal energy difference the value of $\Delta h - (u_2 - u_1)$ for friction approach will exactly the same with the value of Δh . This implies that P2 will be smaller for friction approach than for constant internal energy due to the factor of density ρ_2 which decreases much for friction approach. Even if both of values above is not equal, says the value from friction approach larger than constant internal energy, the product of this value with ρ_2 may still yield smaller P2 for friction approach method.

This logic could explain why the temperature is higher but the pressure is lower at the bottom of pipe when comparing two approaches provided in this section.

3.3.5 Comparison all approaches with commercial software's

The commercial software's that we are going to use for comparing with the approaches provided in this work are:

- IPM-PROSPER

For this software we have many options of correlation to estimate the pressure distribution along the tubing/vertical pipe. The tubing correlations below are used for comparison:

- Gray
- Hagedorn-Brown
- Beggs-Brill
- Pet. Exp. 4
- Petroleum Experts

- UNISIM

We use Soave-Redlich-Kwong equation of state to calculate the fluid properties.

For IPM-PROSPER, we set the overall heat transfer coefficient to 0.0000001 in order to represent the adiabatic condition and we used the rough approximation method. This setting causes the temperature only slightly increase from the initial injection temperature and can be assumed constant for practical purposes. Even though the temperature is almost constant but the pressure profile predicted by this software is “quite close” to our approaches and also method from other software. We don't really sure how pressure and temperature related in the calculation of this software. So we just only present the pressure profiles from this software with correlations mentioned above but we don't present temperature profiles for comparison.

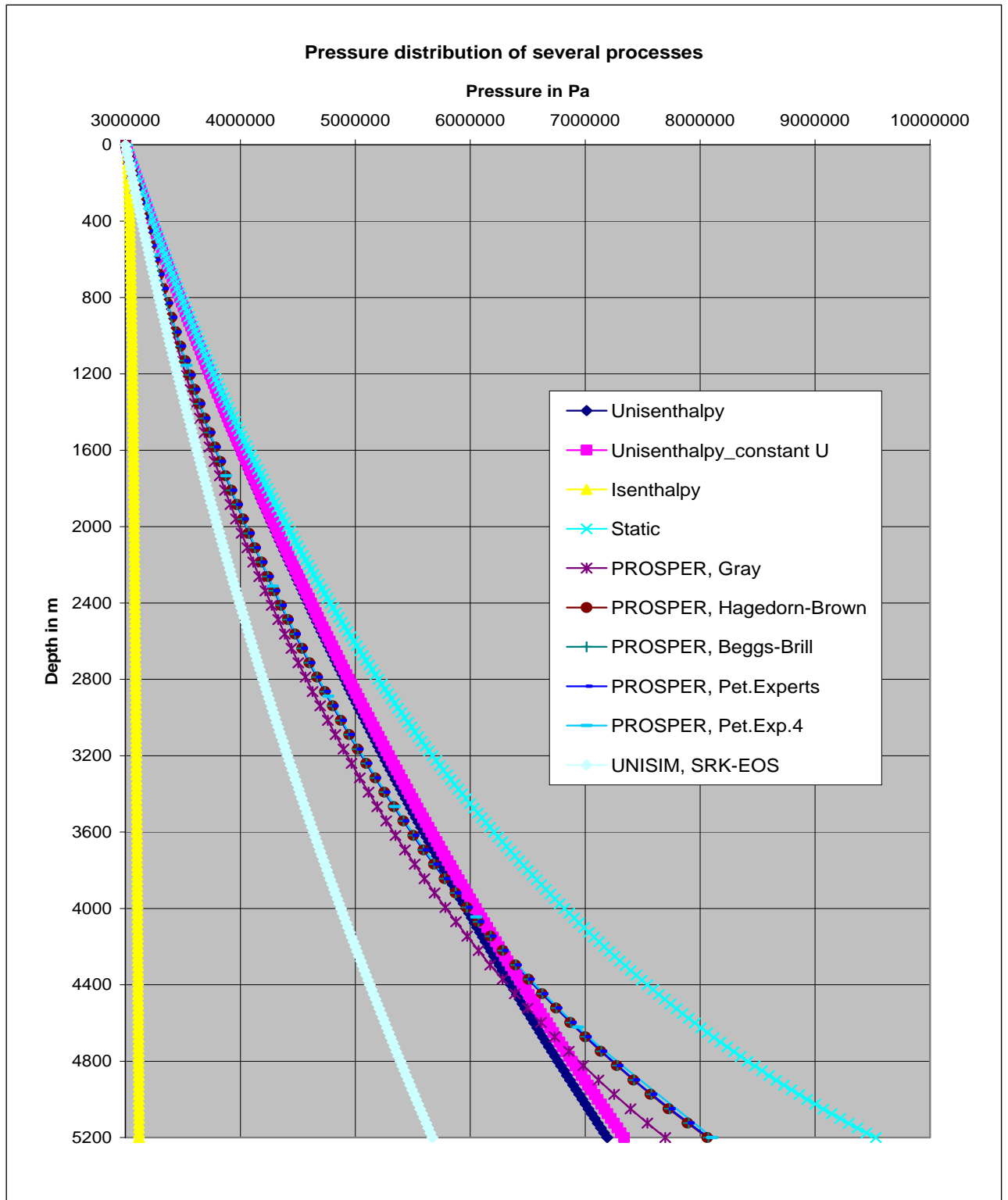


Fig. 3.3.5.1 Pressure profile comparison between all approaches and commercial software's

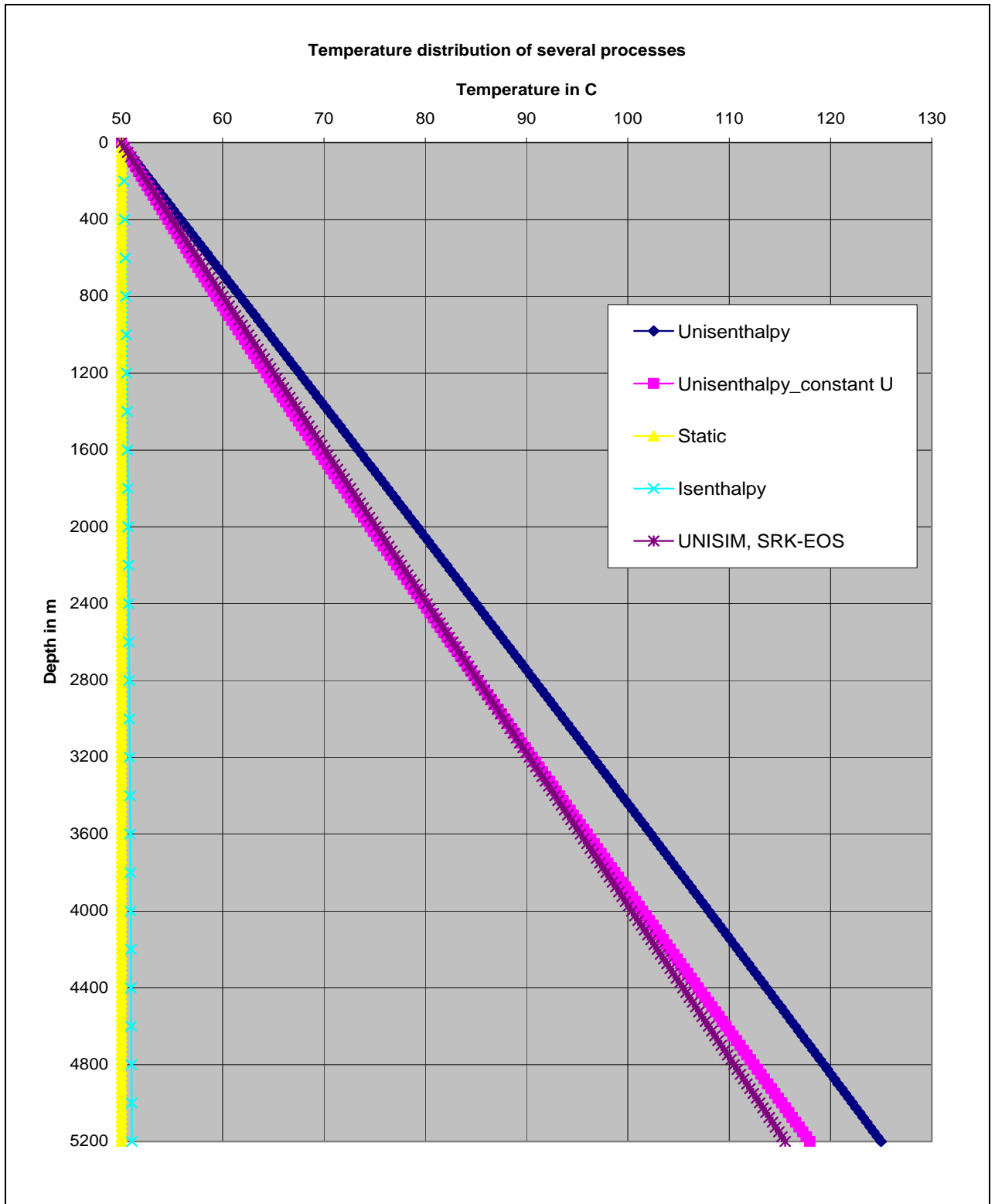


Fig. 3.3.5.2 Temperature profile comparison between all approaches and commercial software's

The graphs above can be summarized in the table below which contains only the top and bottom state:

Injection case	Pressure		Temperature		Pressure Percent error*
	P_top	P_bottom	T_top	T_bottom	
Static case	30	95.288	50	50	
Isenthalpy	30	31.185	50	51.04	
Unisenthalpy-friction approach	30	71.912	50	124.984	
Unisenthalpy-constant Int. En.	30	73.386	50	117.957	2.05
UNISIM-SRK	30	56.707	50	115.53	-21.14
PROSPER, Gray	30	76.96			7.02
PROSPER, Hagedorn-Brown	30	80.61			12.1
PROSPER, Beggs-Brill	30	80.73			12.26
PROSPER, Petroleum experts	30	80.73			12.26
PROSPER, Pet. Exp. 4	30	81.04			12.69

Table 3.3.5 Comparison between all approaches and Commercial software's

*Unit of pressure is bara and unit of temperature is °C. * sign refers to the unisenthalpy-friction approach as the reference.*

With the reference of unisenthalpy-friction approach, we observe that PROSPER gives the pressure percent error about 12 – 13 %. The lowest error is the calculation with Gray correlation. UNISIM gives the underestimate value of bottom pressure about -21 % from the reference value.

3.3.6 Unsteady state Isothermal filling

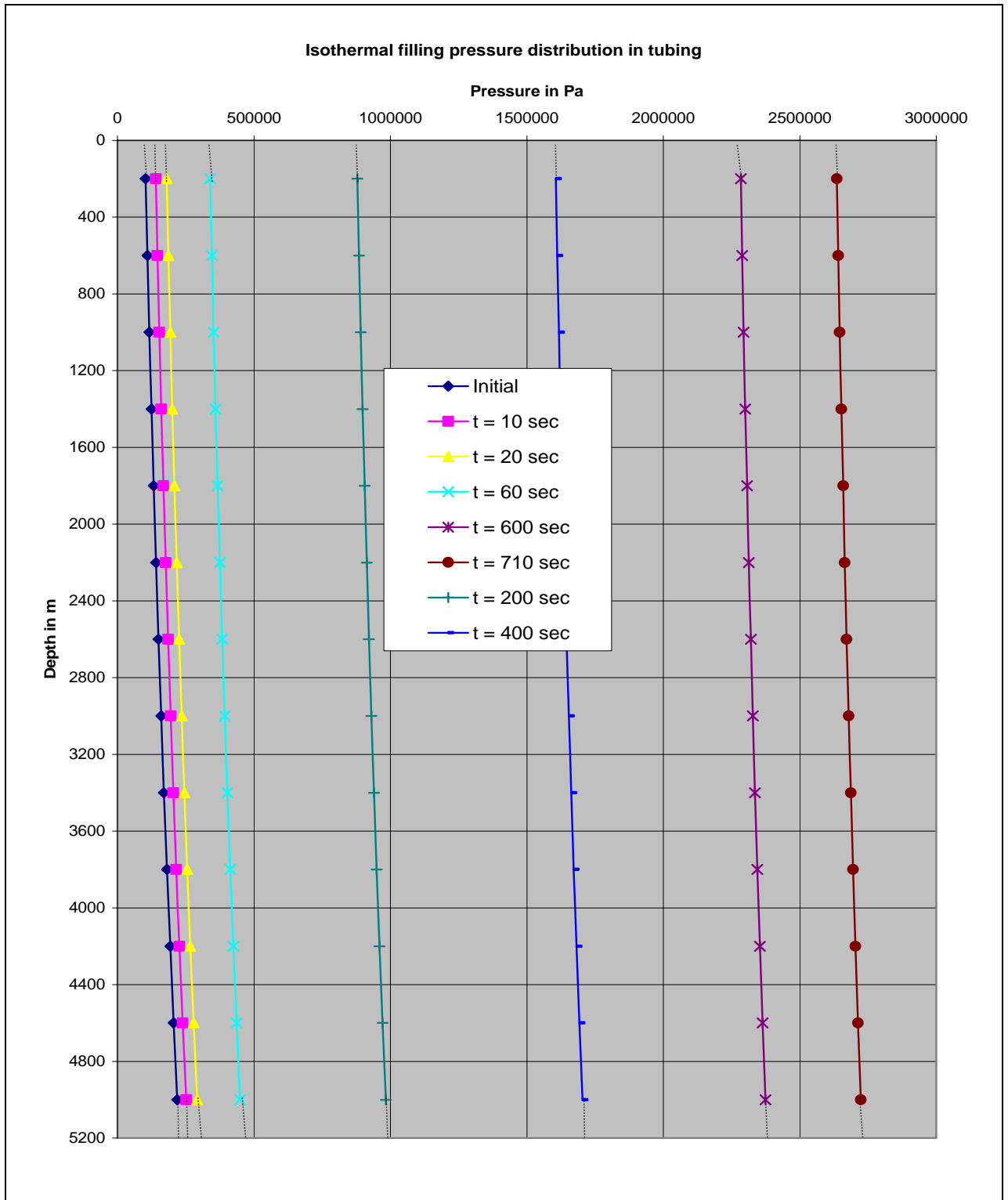


Fig. 3.3.6 Transient pressure profile of Isothermal filling method

Transient pressure profile above is obtained with assumption of injection fluid accumulation in the tubing is distributed homogeneously along the tubing. The compressibility factor of each pipe segment is calculated, afterward the pressure can be calculated as the function of compressibility factor and temperature. Thus temperature has to be known/specified before (e.g. for our case is assumed isothermal).

If the heterogeneous distribution occurs, calculation with this method needs input of mass distribution along the pipe for every time step (i.e. the mass distribution as the function of time). It means more information is needed to be able to calculate with this method.

For non-isothermal case, again, we need input of temperature distribution along the pipe for every time step in order to be able to calculate with this method. The temperature in this method is assumed independent of pressure. After the temperature is set, the calculation of pressure can be done.

To be able to calculate transient pressure, boundaries are needed. Transient pressure calculation starts at initial condition where every properties and parameters are known and will be end when the certain condition is reached. For example, our case starts with isothermal static condition with surface pressure and temperature are 30 bara and 50 °C respectively. The calculation can be continued to any time we want but surely we need to stop at sometime. So we have to put the boundary for it (e.g. for our case, the final boundary is the bottom hole valve opening pressure i.e. 27.3 bara).

The graph shows that for the time of 710 seconds, the bottom pressure reaches 27.3 bar. So the time needed from the starting of filling until the time of the flow starts is 710 seconds.

3.3.7 Unsteady state pressure profile based on linearity

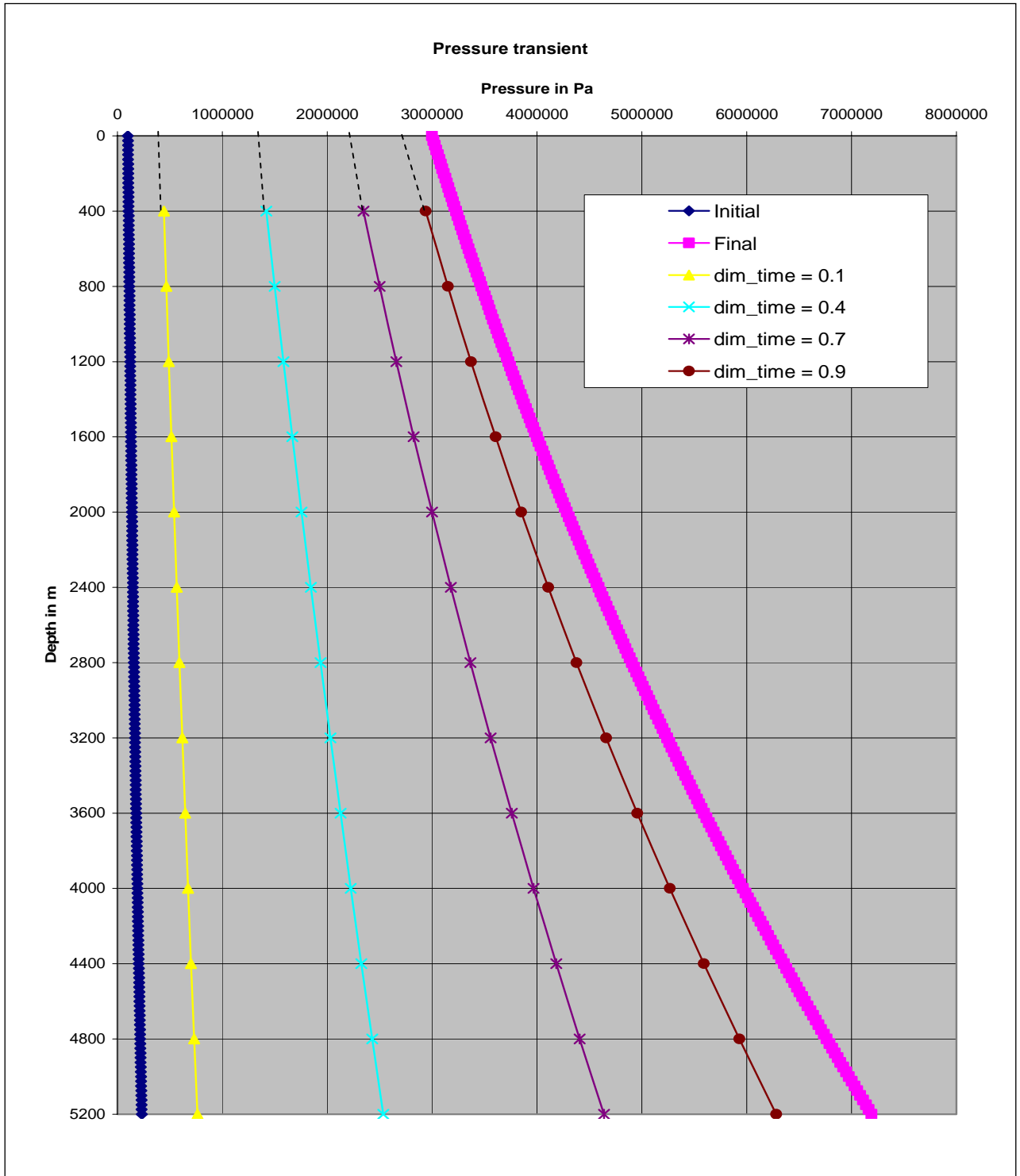


Fig. 3.3.7 Transient pressure profile of simple approach based on linearity.

This method assumes that the temperature profile and internal energy along the pipe act linearly with respect to time. Thus, temperature and internal energy for every time and location in the pipe are known. Using both, we can calculate the pressure for every time and every location in the pipe.

The method can be used as long as the boundary conditions are known (e.g. for our case the boundaries are isothermal static with surface pressure and temperature 1 bara and 50 °C as initial boundary and steady state at surface pressure and temperature 30 bara and 50 °C).

This method may be insufficient to estimate the real transient pressure profile due to the assumptions that we know in real life, the assumptions are not valid. It aims to give the first estimation of pressure profile as the function of time. Next step is to correct this first estimation until it approaches the real one. The advance method to do correction is not the subject of this work.

4. CONCLUSIONS

Estimation of pressure and temperature profile along the pipe for Adiabatic steady state injection flow need at least three equations, named: continuity equation, momentum equation and energy balance equation. Energy balance equation relates between the fluid properties (i.e. density, viscosity, enthalpy, internal energy, JT-coefficient and entropy) and injection parameters (i.e. mass rate injection, pipe diameter, pipe roughness, length of pipe, etc). Energy balance equation shows kinds of energy that the fluid could have (e.g. potential, kinetic, flow work, etc) and the relation for all of them.

For injection case, the change in fluid potential energy due to position will be transferred to fluid temperature, pressure, density and velocity. Density itself is function of pressure and temperature. The correct pressure and temperature has to fulfill the energy balance equation and other relation simultaneously. So, the issue here is how the energy is distributed quantitatively into each kind of fluid energy so they can fulfill all existing relations between them.

Several approaches are proposed in this work to estimate the pressure and temperature profile along the pipe (e.g. isenthalpy flow, unisenthalpy-friction, etc). The closest (but may not be the best) approach to real case is unisenthalpy with friction which the internal energy changes are approximated by energy dissipated by friction. This approach neglects the fluid compressibility. For CO₂, It seems that it is too risky to neglect the compressibility because CO₂ especially at gas phase is compressible. So, further research should be emphasized more to internal energy changes and the method to approximate its value.

The accuracy of CO₂ properties used in the calculation is one of important things to determine the accuracy of pressure and temperature profile prediction. CO₂ properties are found by methods and/or correlations. The use of the “right” one will reduced the inaccuracy of calculation due to properties error.

Density is estimated quite well by almost all equations of state provided in this work but the conceptual properties such as enthalpy, entropy, internal energy, and JT coefficient yield larger error relative to the reference than the measured properties. The reference for these properties is Angus et al. [1] It means uncertainty of these properties is higher as well. This conceptual property plays important role in the calculation, therefore the better methods to estimate these properties are still awaited.

Viscosity can be estimated very well using every correlation provided in this work. Viscosity is involved in pressure and temperature profile calculation by the merit of Reynolds number to estimate the friction factor of flowing fluid. It is shown that the friction factor is weak function of Reynolds number. Thus the viscosity changes do not give significant changes in friction factor which also will not give significant changes to pressure and temperature profile along the pipe. Viscosity is not the only parameter but all the injection parameters involved in friction calculation (i.e. injection mass rate, diameter, and roughness) that the change in it will not give the significant change in pressure and temperature profiles.

The rest properties in this work (i.e. heat capacities and thermal conductivity) are used in injection case with heat transfer which is not the subject of this work. Its value which is predicted by methods in this work gives large error relative to its reference. It implies that the uncertainty in its value as the function of pressure and temperature is high. Thus, the better methods in predicting those properties are still needed.

Multiphase correlations for calculating pressure drop when used for single phase pressure drop calculation by some commercial software may not yield good prediction on pressure profile and temperature profiles. We allege that the cause of it mainly due to combination between limitation in properties determination, correlations and relation between pressure and temperature in the approach to obtain temperature and pressure profiles.

For injection case at unsteady state/transient period, the pressure profile calculation needs information of other parameter and/or properties (e.g. mass accumulation, temperature, etc) as a function of time. The calculation also needs the boundaries where the calculation starts and ends. When those information are absent, “linearity” is be used to give the rough approximation, for example to the pressure profile. As an example to this is the calculation at transient case.

5. DEVELOPMENT POSSIBILITY

Humbly we realize that this work is far from perfect, also the big picture of this work is not yet accomplished. In fact this work is only small part in the beginning of effort to understand deeper the real CO₂ injection processes. Our understanding is just started and need to be increased by further research, observation, experience, idea and advice/suggestion from experts in this subject.

After the work we have done, we felt that some interesting things can be develop and could be very exciting topic for the next work in the future. Some of those are

- Advance research on CO₂ conceptual properties such as Enthalpy, Entropy and Internal energy.
- Development of Adiabatic steady state flow especially on internal energy difference term in energy balance equation. Both entropy and compressibility of fluid are to be considered together and simultaneously.
- Development to injection case with heat exchange with surroundings. In real life heat transfer phenomenon always occur anywhere and everywhere.
- Development to fluid mixtures. CO₂ to be injected into reservoir usually would not be in pure condition but some impurities exist. This would makes a bit complicated an tedious on fluid properties part but it's surely very challenging
- Development to other geometry of well/pipe than vertical one and may be also the combination of several pipe diameters.
- Development to multiphase injection flow. In this work, we just consider the single phase flow as recommended by TOTAL but the phase change always have the chance to occur somewhere along the tubing/pipe.

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NOMENCLATURE

A	Area
C _p	Constant pressure specific heat
C _v	Constant volume specific heat
C _p [*]	Ideal specific heat at constant pressure
D	Diameter of pipe/tubing
EOR/IOR	Enhanced oil recovery/Improved oil recovery
f	Friction factor
<i>f</i>	Specific Helmholtz energy
<i>f</i> [*]	Specific Helmholtz energy at ideal condition
g	Gravity acceleration
<i>h</i>	Specific enthalpy
<i>h</i> [*]	Specific enthalpy at ideal condition
<i>k</i> or λ	Thermal conductivity
<i>m</i>	Mass rate
M	Molecular weight
MGR	Residual gas management
n	Molar mass
P/p	Pressure
P _c	Critical pressure
P _r	Reduced pressure, P/P _c
\dot{Q}	Total mass rate exchanged between system and surroundings
R	Gas constant
Re	Reynolds number
S	Entropy
<i>s</i>	Specific entropy
<i>s</i> [*]	Specific entropy at ideal condition
T	Temperature
T _c	Critical temperature

T_r	Reduced temperature, T/T_c
t_{ss}	Time to reach steady state condition from initial condition
t_d	Dimensionless time, t/t_{ss}
t	Time
U_{cv}	Extensive control volume internal energy
u	Specific internal energy
u^*	Specific internal energy at ideal condition
v	Specific volume
v^*	Ideal specific volume
V	Velocity
\dot{W}	Total work per unit time exchanged between system and surroundings
z	Compressibility factor
$z_{i/e}$	Vertical depth relative to depth
ρ	Density
η_0	Low pressure viscosity
η or μ	Viscosity
ε / D	Dimensionless roughness
μ_{JT}	Joule-Thomson coefficient

EXAMPLES OF PROGRAM CODE IN MATLAB FILE

1. Calculation of density from Patel-Teja Equation of state

```

% Patel and Teja (1982) Equation of State
% Calculating the density /specific volume of Carbondioxide

T = input('Type in the temperature in deg. C: ');
P = input('Type in the pressure in bar: ');

R = 83.145; T = 273.15+T; Tc = 304.12; Pc = 73.74;
Tr = T/Tc; Pr = P/Pc; omega = 0.225; M = 44.011; Vc = 94.07;

%eps = Pc*Vc/R/Tc;
eps = 0.329032 - 0.076799*omega + 0.0211947*omega^2;
to_c = 1 - 3*eps;

k = [1, 2 - 3*eps, 3*eps^2, -(eps^3)];
v = roots(k);
if imag(v(2,1)) == 0
    v = sort(v);
elseif imag(v(1,1)) == 0
    v = [v(1,1); v(1,1); v(1,1)];
else
    v = [v(3,1); v(3,1); v(3,1)];
end
to_b = v(1,1);

to_a = 3*eps^2 + 3*(1 - 2*eps)*to_b + to_b^2 + 1 - 3*eps;

F = 0.452413 + 1.30982*omega - 0.295937*omega^2;

alfa = (1 + F*(1 - Tr^0.5))^2;
a = to_a*(R^2)*(Tc^2)*alfa/Pc;
b = to_b*R*Tc/Pc;
c = to_c*R*Tc/Pc;

l = [P, P*c - R*T, -P*b^2 - 2*b*c*P - b*R*T - c*R*T + a, c*P*b^2 + b*c*R*T - a*b];
w = roots(l);

disp(' The density in mol/dm3 is ');
dens1 = 1000/w(1,1)
dens2 = 1000/w(2,1);
dens3 = 1000/w(3,1)

```

2. Calculation of Internal energy from Peng-Robinson equation of state

% Calculation of the differences of enthalpy and entropy between
%two states for Carbondioxide only

```
%disp(' State 1 ')
T1 = 26.85;
P1 = 1;
%disp(' State 2 ')
T2 = input('Type in the temperature T2 in deg. C: ');
P2 = input('Type in the pressure P2 in bar: ');
```

```
M = iedepfunc(T1, P1);
N = iedepfunc(T2, P2);
u1 = id_intenergy(T1, P1);
u2 = id_intenergy(T2, P2);
```

```
u2u1_1 = M(1,1) - N(1,1) + (u2 - u1);
u2u1_2 = M(1,1) - N(1,2) + (u2 - u1);
u2u1_3 = M(1,2) - N(1,1) + (u2 - u1);
u2u1_4 = M(1,2) - N(1,2) + (u2 - u1);
```

```
disp('The internal energy difference in J/mole is')
u2u1_1; u2u1_2; u2u1_3, u2u1_4,
```

Subroutine of “iedepfunc”:

% Subroutine Internal energy departure function from Peng-Robinson equation

```
function U = iedepfunc(T, P);
```

```
R = 8.3145; T = 273.15+T; P = P*1e5; Tc = 304.12; Pc = 73.74*1e5;
Tr = T/Tc; Pr = P/Pc; omega = 0.225; M = 44.011; Vc = 94.07;
```

```
fw = 0.37464 + 1.54226*omega - 0.26992*(omega^2);
ac = (0.45724*(R*Tc)^2)/Pc;
alpha = (1 + fw*(1 - Tr^0.5))^2;
a = ac*alpha;
b = 0.07780*R*Tc/Pc;
```

```
k = [1, b - R*T/P, -(3*b^2 + 2*b*R*T/P - a/P), b^3-a*b/P+(b^2)*R*T/P];
v = roots(k); v = sort(v);
```

```

v_id = R*T/P; B = 0.0778*Pr/Tr;

z1 = v(1,1)/v_id; z2 = v(3,1)/v_id;

%disp('The enthalpy departure function in J/mol is ')
eh1 = -R*Tc*(Tr*(z1 - 1) - 2.078*(1 + fw)*(alpha^0.5)*log((z1 + 2.414*B)/(z1 -
0.414*B)));
eh2 = -R*Tc*(Tr*(z2 - 1) - 2.078*(1 + fw)*(alpha^0.5)*log((z2 + 2.414*B)/(z2 -
0.414*B)));

%disp('The internal energy departure function in J/mol is ')
ie1 = eh1 - P*(v_id - v(1,1));
ie2 = eh2 - P*(v_id - v(3,1));

U = [ie1 ie2];

```

Subroutine of “id_intenergy”:

```

% Calculation of ideal enthalpy for Carbondioxide

function [idie] = id_intenergy(T,P)

T = 273.15 + T; R = 8.3145; P = P*1e5;
A = 19.8; B = 7.344*1e-2; C = -5.602*1e-5; D = 1.715*1e-8;

%disp('Ideal gas enthalpy in J/mol is ')
h_i = (A*T + (B/2)*(T^2) + (C/3)*(T^3) + ...
(D/4)*(T^4));

v_i = R*T/P;

u_i = h_i - P*v_i;

idie = u_i;

```

3. Calculation of pressure profile in Isothermal Static scene

```

P_in = input('Type in the surface/top pressure in bar absolute: ');
T = input('Type in the temperature in C : ');
H = input('Type in the length of the vertical pipe m: ');
d = input('Type in the diameter of tubing in inch : ');

d = d*0.0254; A = 0.25*pi*d^2;

h_strt = 0;
h_end = H;
N = 13;
h_incr = (h_end - h_strt)/N;

Pst = P_in;
h = h_strt;
h_mid = h_strt + h_incr/2;
m_st = 0;

RH = [];
DE = [];
PR = [];
MS = [];
EH = [];
IE = [];

rho = PRdens(T, Pst);
g = gravacc(h_mid);
h_int = h_strt + h_incr;
P_strt = Pst*1e5;

for i = 1:N
    P_calc = P_strt + rho*g*h_incr;
    m = m_st + rho*A*h_incr;
    P_cal = P_calc*1e-5;
    rhonext = PRdens(T, P_cal);
    inenext = int_energy(T, P_cal);
    enthnext = enthdatum(T, P_cal);
    h_mid = h_mid + h_incr;
    P_strt = P_calc;
    rho = rhonext;
    g = gravacc(h_mid);
    hn = h + h_incr;
    h = hn;
    m_st = m;

```



```
RH(i,1) = rho
EH(i,1) = enthnext;
IE(i,1) = inenext;
DE(i,1) = h;
PR(i,1) = P_strt
MS(i,1) = m
end
```

```
disp('The mass in the tubing in kg is : ')
mass = m_st
```