

# The Exergy of Geothermal Fluids: CO<sub>2</sub> versus Water

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## ABSTRACT

Since exergy is a measure of the maximum amount of the mechanical work that an energy carrying fluid at a given temperature and pressure can possibly deliver, we evaluate the exergy carried by CO<sub>2</sub> as it circulates through a hot rock reservoir and compare with that evaluated for water to determine what fluid, CO<sub>2</sub> or water, offers better functionality in geothermal heat extraction. The results indicate that the total exergy flow carried by CO<sub>2</sub>, in general, is 4.3 to 15.7 times higher than that for water, depending on the temperature and the pressure. It is also observed that, on a comparative analysis, more mechanical work can be converted from a reservoir with low temperature and low pressure.

## 1. Introduction

Geothermal energy refers to the thermal energy naturally stored in the hot rock formation buried deep beneath the Earth's surface. To harvest this source of energy both water and CO<sub>2</sub> have been used as the heat extraction fluids [Hadu et al. (2016), Shaik et al. (2011), Zeng et al. (2013), Brown (2000), Pritchett (2009), Xu and Pruess (2010), Pruess and Spycher (2010), Xu et al. (2015), Randolph and Saar (2011), Pruess (2006 & 2008)]. It is summarized from these reports that use of water for geothermal heat mining has many disadvantages due to its powerful chemical properties as a solvent for many rock minerals, especially at elevated temperatures. Water is corrosive, and as it flows, it corrodes or scales the reservoir's flow pathway as well as piping and the turbine blades, especially if it is saturated with minerals. Moreover, in many regions, water is a sparse and valuable commodity; in arid regions water losses during fluid circulation can present a significant economic liability and burden. On the other hand, using CO<sub>2</sub> as the geothermal extraction fluid seems to have many advantages. It is a non-polar fluid with low salt solubility. Thus, use of CO<sub>2</sub> can reduce the likelihood of mineral precipitation in wellbores and surface equipment. More importantly, unlike water, CO<sub>2</sub> has low surface tension, meaning it can flow easily through small pores and fractures that would be clogged by water molecules. Thus, CO<sub>2</sub> can be circulated through a reservoir with lower permeability and with

less pumping power. CO<sub>2</sub> can be used to extract heat from a geologic formation with lower temperature, which can translate into shallower wells with lower costs. With lower viscosity, CO<sub>2</sub> offers the possibility of less hydraulic-fracturing which is expensive. Direct use of produced CO<sub>2</sub> fluid in turbomachinery is also possible. In addition to these obvious advantages, use of CO<sub>2</sub> for geothermal heat extraction is also a means for physical sequestration of some CO<sub>2</sub> used.

In addition to the disadvantages and advantages mentioned above, Pruess (2006) also provided a comprehensive analysis to compare the energy recovery rates between water and CO<sub>2</sub> based on their thermal and physical properties. In this paper we will evaluate the exergy carried by CO<sub>2</sub> and water as they circulate through a hot rock reservoir in order to compare their performances in geothermal heat extraction applications. We use the concept of exergy since the heat content of a geothermal fluid, in terms of its enthalpy, is only a partial measure of the total energy within the system that could be converted into useful work. Heat content, therefore, is not a complete measure of the useful work that the flowing fluid can deliver. The exergy of a system is defined as the maximum amount of the mechanical work that an energy carrying fluid at a given temperature and pressure can deliver, from its enthalpy, when it is allowed to interact with a given environment [Bejan (2006)]. Thus, exergy represents a more direct measure of the mechanical work available at a given thermodynamic condition.

## 2. Flow Exergy

We consider the flow of a heat extraction fluid having a temperature  $T$ , pressure  $P$ , and mass flow rate  $\dot{m}$ , circulating through a hot rock reservoir. To determine the exergy of this fluid we allow it to expand through a reversible engine producing a shaft work  $\dot{W}_{shft}$  and rejecting  $\dot{Q}_E$  heat into an environment of temperature  $T_o$  and pressure  $P_o$  as shown in Fig. 1. To maximize the work output, the rejected heat  $\dot{Q}_E$  is used to run a reversible Carnot heat engine producing an additional work  $\dot{W}_E$ . Since the reservoir depth and pressure are constant, the potential and kinetic effects are neglected and the First law of thermodynamics states that:

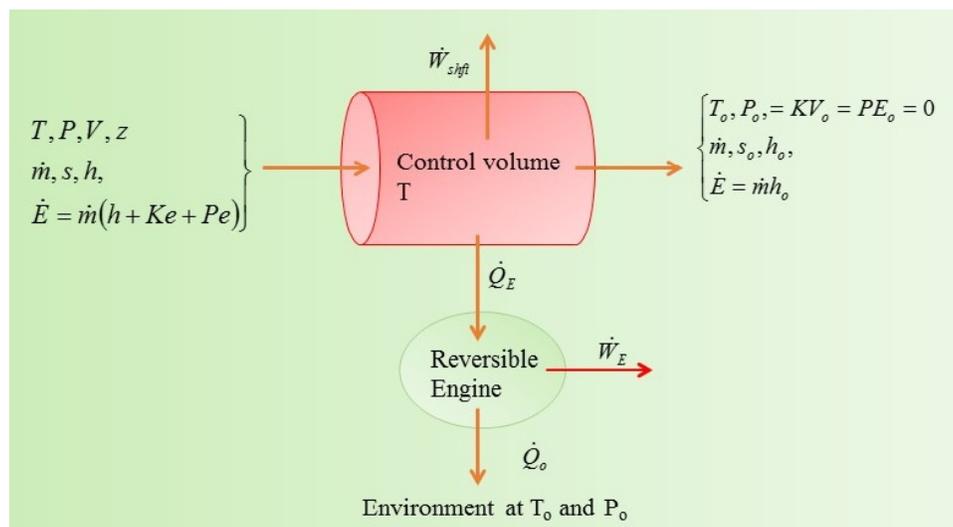


Figure 1. Representation of the system-environment composite for exergy analysis

$$\dot{W}_{shft} = \dot{m}(h - h_o) - \dot{Q}_E \quad (1)$$

Where  $h$  is the fluid enthalpy at  $T$  and  $h_o$  is the fluid enthalpy at  $T_o$ . The additional work produced from the Carnot heat engine is

$$\left. \begin{array}{l} \frac{Q_E}{T} = \frac{Q_o}{T_o} \\ \dot{W}_E = \dot{Q}_E - \dot{Q}_o \end{array} \right\} \Rightarrow \dot{W}_E = Q_E \left( 1 - \frac{T_o}{T} \right) \quad (2)$$

And the total work is

$$\dot{W} = \dot{W}_{shft} + \dot{W}_E = \dot{m}(h - h_o) - \frac{T_o Q_E}{T} \quad (3)$$

From the Second Law of thermodynamics

$$\dot{\sigma}_{gen} = \dot{m}(s_o - s) + \frac{\dot{Q}_E}{T} \quad (4)$$

Where  $\dot{\sigma}_{gen}$  is the entropy production,  $s$  is the fluid entropy at  $T$  and  $s_o$  is the fluid entropy at  $T_o$ . Thus

$$\dot{W} = \dot{m}(h - h_o) - T_o \dot{\sigma}_{gen} + \dot{m}T_o(s_o - s) \quad (5)$$

For the work, given by equation (5), to be maximum, the process must be reversible, that is, the entropy generation must be zero,  $\dot{\sigma}_{gen} = 0$ . Then, the flow exergy is

$$\dot{E}_x = \dot{W}_{max} = \dot{m}[h - h_o - T_o(s - s_o)] \quad (6)$$

### 3. Thermo-physical Properties

In this paper the simple but accurate correlation equations reviewed in Phuoc et al (2017) for calculating the thermal and transport properties of water and CO<sub>2</sub> are used. Using these equations, deviations from values obtained from the NIST web database (2007) were evaluated for the calculated density, enthalpy, entropy, specific heat, viscosity, and thermal conductivity of water and CO<sub>2</sub> for temperatures from 300 to 600 K and pressures up to 60 MPa. For water, the average deviations were found to be negligible for all the properties. For CO<sub>2</sub>, average deviations of about 0.2% to 2.5% were obtained for the thermal conductivity, less than 0.1% for all other properties. Thus, the empirical equations reviewed by Phuoc et al. (2017) can accurately predict the thermo-physical properties of both CO<sub>2</sub> and water under the pressure and temperature condition practically found in geothermal heat extraction applications.

#### 4. Results and Discussions

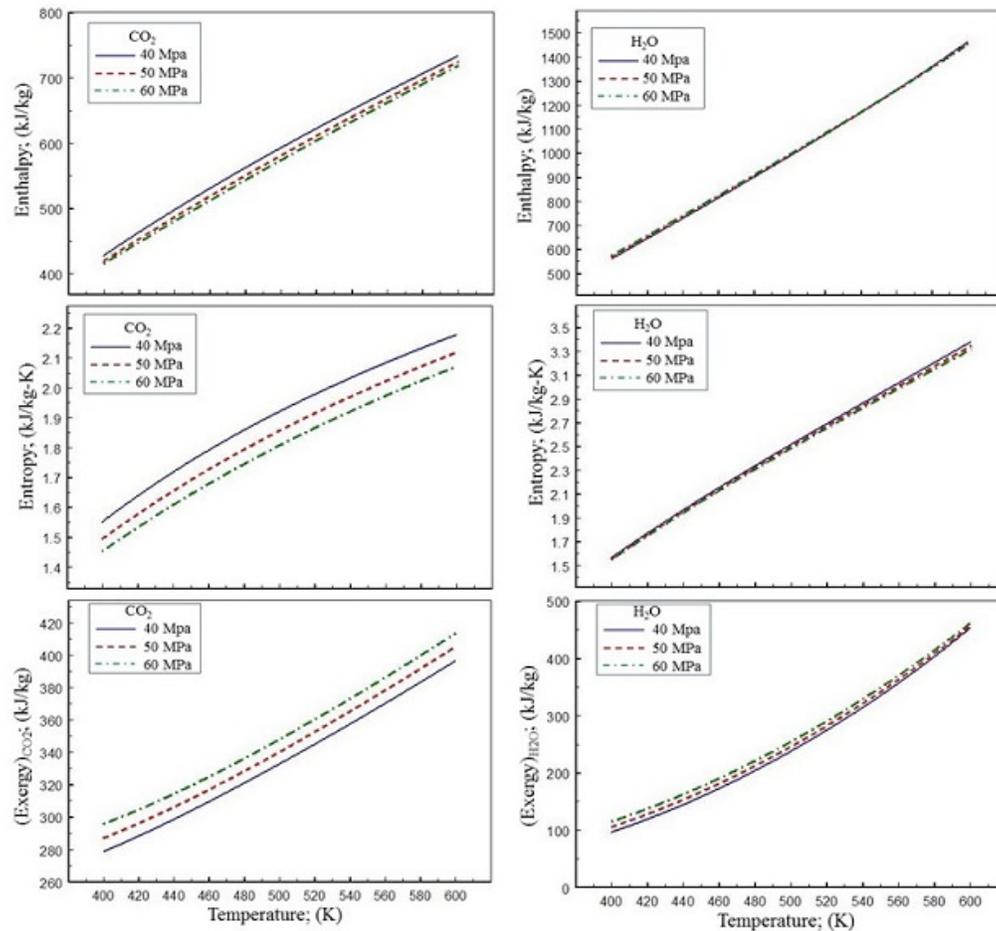
To calculate the exergy of a working fluid we use the environment temperature  $T_o = 300$  K and pressure  $P_o = 1$  atm (the corresponding properties for  $\text{CO}_2$  are  $h_o = 507.43$  kJ/kg and  $s_o = 2.7446$  kJ/kg-K and for water  $h_o = 112.65$  kJ/kg and  $s_o = 0.39306$  kJ/kg-K). The temperatures ranging from 400 K to 600 K and pressures from 40 to 60 MPa are used as the operating conditions at the bottom of the production well. The results are shown in Fig. 2. Both the enthalpy and the entropy of water are nearly independent of pressure over the range of interest but increase significantly with increasing temperature. The entropies of water reported here for the bottom well conditions of interest range from about 1.5 kJ/kg-K to about 3.4 kJ/kg which are higher than the entropy of water at the environment conditions,  $s_o = 0.39306$  kJ/kg-K. For  $\text{CO}_2$ , these properties are significantly lower than those calculated for water and they decrease as pressure increases but increase as temperature increase. The calculated  $\text{CO}_2$  entropies for all conditions are seen to be lower than  $s_o = 2.7446$  kJ/kg-K given at  $T_o$  and  $P_o$ . The enthalpies of water range from about 560 kJ/kg to about 1450 kJ/kg, while the values for  $\text{CO}_2$  range from 425 kJ/kg to about 710 kJ/kg for the range of temperatures used here. The important result shown here is that although the water specific enthalpy is about 1.2 to 2 times higher than that of  $\text{CO}_2$  across the temperature range of interest, the  $\text{CO}_2$  specific exergies are higher across most of this range, varying from three times higher at 400 K and 40 MPa to only 0,8 times as high at 600 K and 40 MPa. Thus, the potential for  $\text{CO}_2$  as a working fluid to be used to convert the hot rock energy into useful mechanical work is significantly higher than that of water.

In Fig. 3 we show the ratio of the total flow exergy calculated for  $\text{CO}_2$  as a working fluid to that calculated for water as a working fluid. To obtain these results, we use the injection temperature of 320 K (as a bottom hole condition in the injection well), and reservoir pressures of 40 MPa, 50 MPa, and 60 MPa. The temperature at the bottom of the production well varies from 400 K to 600K. The flowrate entering the reservoir is determined using the conditions at the bottom of the injection well. Since the (mass) flowrate is proportional to  $(\rho/\mu)(dp/dx)$ , for the same pressure gradient,  $dp/dx$ , the ratio of  $\text{CO}_2$  mass flowrate to water mass flowrate is  $\dot{m}_{\text{CO}_2}/\dot{m}_{\text{H}_2\text{O}} = (\rho/\mu)_{\text{CO}_2}/(\rho/\mu)_{\text{H}_2\text{O}}$ . We tabulate the conditions at the injection well in Table 1.

The results shown in Fig. 3 indicate that the total exergy for  $\text{CO}_2$  as the working fluid in a hypothetical reservoir, is 4.3 to 15.7 times higher than that for water as the working fluid depending on temperature and pressure. It is also noticed that substantially more mechanical work could be converted from a reservoir with low temperature and low pressure by using  $\text{CO}_2$ .  $\text{CO}_2$  has much less surface tension and is able to flow through smaller pores. Thus,  $\text{CO}_2$  can be used to extract heat from low permeability geologic formation at less depth where lower temperatures are found. Thus  $\text{CO}_2$  is a more effective fluid for heat extraction in mining and geothermal applications.

The exergy data presented in Fig. 3 is calculated for the conditions at the bottom of the production well. In practice, the fluid must be pumped or pushed up to the surface where it can be used in a turbine to generate useful mechanical work. The appropriate conditions used to calculate the flow exergy should include those at the production wellhead and at the turbine outlet. Thus, to calculate the flow exergy including these conditions, we use a turbine exit temperature of 313 K (40 C) and pressure of 1 atm. The temperature and pressure at the wellhead

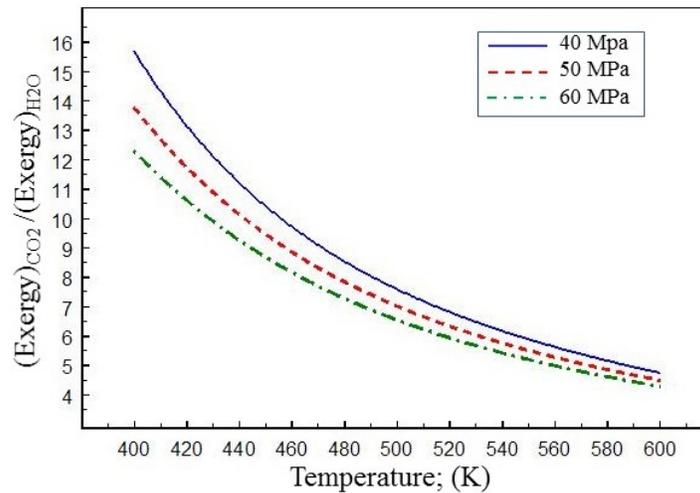
are calculated using the conditions at the well bottom. As the fluid flows up in the production well its temperature and pressure will decrease with depth due to heat loss to the surrounding rock, friction at the walls, fluid decompression and gravitational effects, etc. For the present work, we simply assume that the flow is isentropic and the variation in the pressure is due to the gravitational effect only. With such approximation, the pressure at any depth is calculated by  $P_{y+\Delta y} = P_y - \rho_y g \Delta y$ . Once the pressure  $P_{y+\Delta y}$  is known, the fluid temperature  $T_{y+\Delta y}$ , density  $\rho_{y+\Delta y}$ , and enthalpy  $h_{y+\Delta y}$  are obtained from the known pressure  $P_{y+\Delta y}$  and  $s_{y=-5000}$  which is kept constant throughout the well. In this approach, we perform upward calculations for pressure, temperature, and other properties starting from the well bottom at an initial depth of  $y = -5000$  m to the wellhead ( $y = 0$ ). The temperature  $T = 473$  K and the pressure  $P = 52$  MPa and  $P = 60$  MPa are used for the well bottom condition. The results are shown in Fig. 4 and summarized in Table 2. For these conditions, the specific exergies associated with the CO<sub>2</sub> stream are about two times higher than those associated with the water stream. Since the mass flowrate of the CO<sub>2</sub> is about 5 times higher than that of the water for the same driving force, the amount of useful mechanical work extracted from the heat content in a rock reservoir could be up to ten times more if CO<sub>2</sub> instead of water is used as the heat extraction fluid.



**Figure 2** Specific enthalpy, entropy and exergy of CO<sub>2</sub> and water calculated using the temperature at the production well ( $T_0 = 300$  K,  $P_0 = 1$  atm, with  $h_0 = 507.43$  kJ/kg and  $s_0 = 2.7446$  kJ/kg-K for CO<sub>2</sub> and  $h_0 = 112.65$  kJ/kg and  $s_0 = 0.39306$  kJ/kg-K for water)

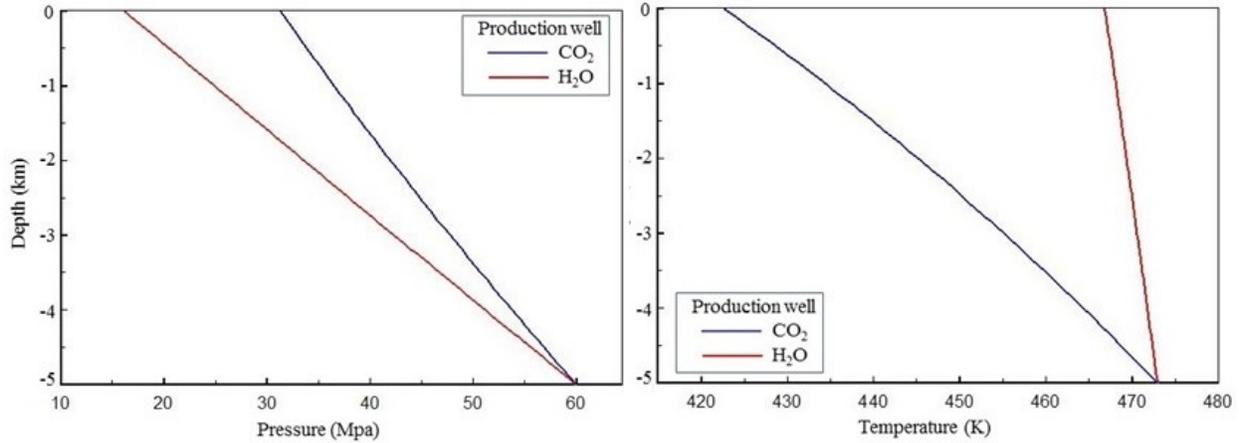
**Table 1. Comparison of CO<sub>2</sub> flowrate with water flowrate entering a hot rock reservoir**

Pressure (MPa)	CO <sub>2</sub>		Water		$\dot{m}_{\text{CO}_2}/\dot{m}_{\text{H}_2\text{O}}$
	Density (kg/m <sup>3</sup> )	Viscosity (mPa-s)	Density (kg/m <sup>3</sup> )	Viscosity (mPa-s)	
40	933.68	100.04	1006.1	584.27	5.42
50	970.11	110.67	1010.1	586.47	5.07
60	1002.1	121.38	1014.0	588.81	4.79

**Figure 3 Ratio of the total exergy delivered by CO<sub>2</sub> to the total exergy delivered by water for the same driving force and reservoir conditions.**

## 6. Conclusions

We have performed a simple analysis to evaluate and compare the performances of CO<sub>2</sub> and water as heat extraction fluids in geothermal applications. In terms of the flow exergy, we have found that CO<sub>2</sub> offers better functionality in the geothermal heat extraction applications. Although the conditions chosen for the present calculation are typically found in many geothermal heat extraction systems, the calculations were carried out only for the flow across the reservoir and upwards in the production well; the conditions at the well bottom were assumed. In real situations, these temperature and pressure conditions at the bottom of the production well must be those that result as the fluid flows through the reservoir rocks collecting heat and losing pressure. Our continuing work, therefore, will focus on the complete flow circuit through the subsurface and surface components of the system, including the downward flow in the injection well, the circulation through the rock reservoir and the flow upward in the production well.



**Figure 4** Variation of the temperature and the pressure with depth in the production well (at the bottom of the well,  $y = -5000$  m, with  $T_{y=-5000} = 473$  K and  $P_{y=-5000} = 60$  MPa

**Table 2.** Wellhead pressure, temperature and flow exergy. Initial conditions at the bottom of the production well ( $y = -5000$  m, temperature = 473 K)  $T_{y=-5000} = 473$  K and  $P_{y=-5000} = 60$  MPa and the corresponding density and entropy are  $\rho_{y=-5000} = 645.85$  kg/m<sup>3</sup>,  $s_{y=-5000} = 1.7227$  kJ/kg-K for CO<sub>2</sub> and  $\rho_{y=-5000} = 902.89$  kg/m<sup>3</sup>,  $s_{y=-5000} = 2.2493$  kJ/kg-K for water. For  $P_{y=-5000} = 50$  MPa and the corresponding density and entropy are  $\rho_{y=-5000} = 580.66$  kg/m<sup>3</sup>,  $s_{y=-5000} = 1.7713$  kJ/kg-K for CO<sub>2</sub> and  $\rho_{y=-5000} = 897.12$  kg/m<sup>3</sup>,  $s_{y=-5000} = 2.2614$  kJ/kg-K for water

Bttom well Pressure (MPa)	CO <sub>2</sub>		Water		Specific exergy (kJ/kg)	
	Wellhead (y = 0) pressure		Wellhead (y = 0) Temperature		Specific exergy	
	CO <sub>2</sub>	water	CO <sub>2</sub>	water	CO <sub>2</sub>	water
52	26.2	8.5	417	466	289.56	130.5
60	31.5	16.5	422	466	295.97	138.15

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