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# Exergy of air, $CO_2$, and $H_2O$ for use as geothermal fluids

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ABSTRACT

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, a fluid is pumped down in a set of injection wells, circulates through the hot rock and then is collected via a set of production wells for heating or other purposes. The selection of this fluid is an important component of a geothermal system. In this work, we review, evaluate, and develop the fundamental equations that can reliably predict the thermodynamic and the transport properties of air, $CO_2$, and $H_2O$. Using these equations, we characterize and compare the heat extraction and exergy carried by these fluids as they circulate through a hot rock reservoir to determine which fluid offers better functionality for geothermal heat harvesting applications. The results indicate that, in terms of heat extraction and exergy, air is a better fluid compared to $CO_2$ and water.



## 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 a set of wells, called injection well and production well, must be drilled through the hot rock formation to a suitable depth. These wells are arranged in such a way that they are connected with each other through a large area of the hot rock reservoir. A cold working fluid is pumped down into the hot rock via the injection well. It circulates and is heated by the rock formation resulting in a hot fluid that is recovered and transported up in the production well to the Earth's surface for space heating and production of electricity. Conventionally, water has been used as a heat extraction fluid [1–3]. $CO_2$ has been also suggested as a heat extraction fluid in recent studies [4–12]. Although these working fluids have many properties that are suitable for geothermal heat extraction applications, disadvantages and advantages associated with these fluids have been recognized and are summarized in Table 1.

From these reports, it can be seen that use of water for geothermal heat mining has many disadvantages mainly due to its chemical properties as a solvent for many rock minerals, especially at elevated temperatures. In addition, water is corrosive, and as it flows, it corrodes or scales the reservoir's flow pathway as well as the walls of the pipes, the turbine blades, especially when saturated with minerals. Also, 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 $CO_2$ as the geothermal extraction fluid seems to have many advantages. It is a non-polar fluid with low salt solubility. Thus, use of $CO_2$ can reduce the likelihood of mineral precipitation in wellbores and surface equipment. More importantly, unlike water, $CO_2$ has low surface tension, indicating that it can flow easily through small pores and fractures that would be clogged by water molecules. Thus, $CO_2$ can be circulated through a reservoir with lower permeability and with less pumping power. Furthermore, $CO_2$ can be used to extract heat from a geological formation with lower temperature, which can be used in shallower wells with lower costs. With a lower viscosity, $CO_2$ offers the possibility of less hydraulic-fracturing. Direct use of $CO_2$ in turbomachinery is also possible. In addition to these, use of $CO_2$ in geothermal heat extraction is also a means for physical sequestration of some of the $CO_2$ used.

Pruess [6,7] provided a comprehensive analysis comparing the energy recovery rates for water and $CO_2$ based on their thermal and physical properties. It must be mentioned that although energy is conserved, not all the energy is available to do useful work. Thus, the heat content of a geothermal fluid, in terms of its

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**Table 1**
Comparison of $CO_2$ and water as heat extraction fluids for geothermal applications.

| Water | $CO_2$ |
|---|---|
| Use of water in geothermal systems is limited by temperature and pressure (384 °C and 22 MPa). Temperatures above these values cause dissolution of silica, which negatively impacts the geothermal reservoir operation | $CO_2$ is not a solvent and it is possible to operate a geothermal reservoir with $CO_2$ at high temperatures without the problem of silica dissolution |
| Water-rock interactions are important. Dissolving reactions can enhance the porosity and permeability. Dissolved minerals may affect the chemical behavior of the water that can damage piping and surface equipment | Due to the non-ionic behavior of carbon dioxide, dissolution and precipitation of minerals are unlikely. At the same time, small amounts of water which are dissolved by carbon dioxide can become chemically active, which could lead to dehydration of minerals which would increase porosity |
| Water in geothermal systems contains significant amounts of dissolved minerals and other trace materials such as arsenic, boron, fluoride etc, which could cause environmental problems when flashed to the surface | When $CO_2$ is used small amount of precipitation of dissolved minerals can be left behind in the micro crack pore structure |
| In a geothermal system, about 5% of the fluid is expected to be lost in the reservoir. Since water is a sparse and valuable commodity, this loss of fluid is a steady consumption of the water and results in a severe economic liability | When $CO_2$ is used this loss of fluid is a benefit as far as $CO_2$ storage and sequestration are concerned |
| Another important factor is the life expectancy of the piping and the power generators. Water corrodes and scales the piping and the turbine blades, especially if it is saturated with minerals | Dry $CO_2$ is not corrosive, but in the presence of water, corrosive carbon acid forms. Especially, in bimodal systems or in bimodal states of systems precautions needs to be exercised |
| Water has high surface tension. Small pores may be clogged by water molecules. Thus, a reservoir with high permeability is required for transporting and heat mining by liquid water | $CO_2$ has much lower surface tension and is able to flow through much smaller pores. Thus, $CO_2$ can be used to extract heat from the naturally existing low permeability geologic formation at low depth with lower temperatures |

enthalpy is not a true measure of the useful work that it can deliver. Since exergy of an energy-carrying fluid is the maximum theoretical work obtainable as it expands through an energy conversion device to its dead state [13], it must be used for the evaluation of the mechanical work delivered by a geothermal fluid. In this paper, we will evaluate the exergy carried by $CO_2$, water, and air as they circulate through a hot rock reservoir, and we compare their performances in geothermal heat extraction applications. We include air in our analysis due to the unavailability of both water and $CO_2$ in certain regions or situations. For example, they may need to be pumped and transported to a geothermal power plant located at a distance from the source. Air, however, is available everywhere. In many regions where neither water nor $CO_2$ is available, air might become the only fluid that can be used.

## 2. Governing equations and the constitutive relations

We assume that the motion and the behavior of the geothermal fluid can be described using the traditional methods of continuum mechanics. In the absence of any chemical and electro-magnetic effects, the basic governing equations are the conservation laws for mass, linear momentum, angular momentum, and energy [14].

### 2.1. Conservation of mass (continuity)

The conservation of mass is:

$$\frac{\partial \rho}{\partial t} = div(\rho \boldsymbol{v}) \tag{1}$$

where $\partial/\partial t$ is the partial derivative with respect to time, $div$ is the divergence operator, $\boldsymbol{v}$ is the velocity vector, and $\rho$ is the density of the fluid.

### 2.2. Conservation of linear momentum

Let $\boldsymbol{T}$ represent the Cauchy stress tensor for the fluid, then the balance of linear momentum is:

$$\rho \frac{d\boldsymbol{v}}{dt} = div\boldsymbol{T} + \rho \boldsymbol{b} \tag{2}$$

where $d(.)/dt = \partial(.)/\partial t + [(grad.)]$ is the total time derivative and $\boldsymbol{b}$ stands for the body force.

### 2.3. Conservation of angular momentum

In the absence of couple stresses the Cauchy stress tensor is symmetric, that is

$$\boldsymbol{T} = \boldsymbol{T}^T \tag{3}$$

### 2.4. Conservation of the energy

The energy equation in general can have the form:

$$\frac{de}{dt} = \boldsymbol{T} : \boldsymbol{L} - div\boldsymbol{q} + \rho r + QC_o K_o \tag{4}$$

where e denotes the specific internal energy, **q** is the heat flux vector, r is the radiant heating, Q is the heat of reaction, $C_o$ is the initial concentration of the reactant species, $K_o$ is the reaction rate expression which is a function of temperature, and **L** is the velocity gradient. For most applications where there are no chemical reactions or heat generation, the last term on the right-hand side is ignored. Thermodynamical considerations require the application of the second law of thermodynamics or the entropy inequality. The local form of the entropy inequality is given by Liu [15] as

$$\rho\dot{\eta} + div\varphi - \rho s \geqslant 0 \tag{5}$$

where $\dot{\eta}(x,t)$ is the time derivative of the specific entropy density, $\boldsymbol{\varphi}$ (x, t) is the entropy flux, s is the entropy supply density due to external sources, and the dot denotes the material time derivative. If it is assumed that $\boldsymbol{\varphi} = (1/T)\boldsymbol{q}$ and $s = r/T$, where T is the absolute temperature, then Eq. (5) reduces to the Clausius-Duhem inequality

$$\rho\dot{\eta} + div\left(\frac{\boldsymbol{q}}{T}\right) - \rho\frac{r}{T} \geqslant 0 \tag{6}$$

Even though we do not consider the effects of the Clausius-Duhem inequality in this paper, for a complete thermo-mechanical study of a problem, the Second Law of Thermodynamics must be considered [15–17]. Next, we provide a brief description of the constitutive relations which are needed: the stress tensor **T**, the heat flux vector **q**, and e. We ignore the effects of radiation, r, and the heat of reaction Q.

### 2.5. Constitutive relations

One of the most widely used constitutive relations in fluid mechanics is the Navier-Stokes model, where the stress **T** is explicitly and linearly related to the symmetric part of the velocity