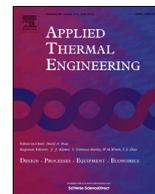




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## Concept for production of chemicals and power using geothermal energy



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### HIGHLIGHTS

- Co-production of power and chemicals using geothermal energy is discussed.
- Process captures energy more efficiently as chemical, sensible and latent heat.
- The co-production process can improve the economics of geothermal energy.
- Novel designs are required for insure safety and guard against contamination.

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### ABSTRACT

This paper presents a concept for conducting commercial chemical reactions and production of power using geothermal heat. The high pressures ( $P_s$ ) and temperatures ( $T_s$ ) that fluids attain in deep reservoirs can be used to manufacture chemicals or decontaminate wastes. High  $P$  reactions which can be expensive and/or unsafe to conduct above ground can be conducted in geothermal reservoirs using closed designs. We present examples of reactions that could benefit from Enhanced Geothermal Systems (EGS) including production of ammonia (NH<sub>3</sub>), supercritical oxidation of wastewater contaminants, production of hydrogen (H<sub>2</sub>) by steam reforming of methanol (CH<sub>3</sub>OH) and partial oxidation of methane (CH<sub>4</sub>) to produce CH<sub>3</sub>OH.

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## 1. Introduction

Geothermal energy is a huge domestic energy resource that is environmentally friendly and can provide baseload capacity to meet customer demands around the clock. It is estimated that geothermal power plants emit only between 19 and 103 g of CO<sub>2</sub>-equivalent per kWh of electricity [10]. By comparison, coal-fired power plants emit about 1235 g of CO<sub>2</sub>-equivalent per kWh of electricity, and natural-gas-fired power plants emit about 487 g of CO<sub>2</sub>-equivalent per kWh of electricity [10]. A recent study by the Massachusetts Institute of Technology [6] estimated that EGS could provide >100,000 MWe in 50 years. At present, geothermal energy is being used for power generation and for industrial and domestic heating applications. Technology to recover energy from EGS is under development.

Presently, many challenges are facing the development of a successful EGS industry including:

- Drilling EGS wells that are deeper than 3000 m is in the experimental stage even though the oil and gas industry has been able to drill deeper wells but in lower temperature environments. Exxon Neftegaz Limited has drilled a well over 11 km deep [3].
- Fracturing of the rock and injecting a fluid to capture the heat are necessary results in excessive water use and loss. Hundreds of millions of gallons of water are required, which will stress competing water demands. For example, a plant that pumps 10 gal/s (38 kg/s) of water and have a 10% water loss will require over 31 million gallons of water per year to compensate for water loss only. This amount is in addition to the water consumed by the power plant.
- Water at high  $T$  and  $P$ , especially supercritical water, is a good solvent for some rock minerals. Dissolved minerals could re-precipitate as the  $T$  and  $P$  fluctuate in the EGS and in the

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pipes, thereby reducing the permeability of the EGS. Fluids that do not interact with the rock minerals could have advantages.

- Seismic activity associated with hydraulic fracturing of EGS reservoirs could be a showstopper in some localities.
- Deep EGS projects, where the  $T$  exceeds about 375 °C, can cause softening of the rocks which causes the rocks to creep and deform, which make it difficult and very costly to maintain the fractures.

Therefore, new concepts and designs may be necessary for more efficient utilization of this energy resource.

The temperatures ( $T_s$ ) and high pressures ( $P_s$ ) required to drive many commercial chemical reactions increases costs and decreases sustainability. Fluids injected in deep and hot Enhanced Geothermal Systems (EGS) reservoirs can reach their supercritical state without expensive and energy intensive mechanical pumping or compression. Supercritical fluids are excellent solvents and efficient media for conducting chemical reactions [4,7,8]. This makes the EGS reservoirs suitable for conducting chemical reactions while at the same time transporting the EGS heat for power generation. Even exothermic reactions require heating to increase their reaction rates. In addition, because the reactions take place underground the cost of the system could be reduced because of less stringent criteria for high  $P$  reactors. Co-production of power and chemicals using EGS reservoirs present a unique business opportunity. Because potential contamination of the underground or of the surface is a major concern both by the chemicals as well as contamination of the reactants and products by materials that may exist in the EGS and to prevent loss of reactants or products, closed system designs are necessary.

In this paper we selected high temperature and high pressure processes that could be considered for use with EGS reservoirs. These are discussed below.

## 2. Production of NH<sub>3</sub>

Ammonia is produced commercially via the reaction ( $3\text{H}_2 + 2\text{N}_2 \rightarrow 2\text{NH}_3$ ) at  $P_s > 150$  bar and  $T_s > 400$  °C. NH<sub>3</sub> synthesis is favored at low  $T$  and high  $P$ . However, high  $T_s$  are used in order to increase the reaction rate. Fig. 1 shows the stoichiometric equilibrium composition for the reaction at different  $T_s$  and  $P_s$ . The process can be carried out at the bottom of the injection pipe of the EGS. A supercritical solution of H<sub>2</sub> and N<sub>2</sub> (at ~200 bar and ~27 °C,

density ~62 kg/m<sup>3</sup>) can be pumped down the injection well of the EGS – supercritical fluids are miscible with each other. Injecting the mixture into a 10 km deep reservoir increases the  $P$  from 200 bar to ~260 bar which increases the NH<sub>3</sub> production by ~15%. (The 10 km depth is used for illustration purposes. The United States Department of Energy is looking at EGS as a significant, low-carbon long term domestic energy source in order to tap into high temperature heat which will result in more efficient power generation.) The products that exit the production pipe of the EGS will be cooled with heat recovery to condense the NH<sub>3</sub>. The unreacted H<sub>2</sub> and N<sub>2</sub> are mixed with makeup H<sub>2</sub> and N<sub>2</sub> and returned to the EGS. About 31 kWh/kmol of NH<sub>3</sub> will be required for producing the supercritical N<sub>2</sub> and H<sub>2</sub> feed. Because less compression is required and heating is supplied by the EGS the cost of NH<sub>3</sub> could be reduced. Fig. 2 is a conceptual design of the process. The heat supplied from the EGS and the heat of the exothermic reaction is recovered by heating the fluid used in the power plant.

The choice of the power plant depends on many factors including the temperature at which the heat is available for power generation and the pressure of the heat carrying fluid and its composition. Conventional steam Rankine power plants, including supercritical plants can be used when the temperature of the available heat at the surface is >375 °C. When hydrogen is a by-product of the reaction it can be separated and for an energy source or for hydrogenation (e.g. at an oil refinery). Hot and high pressure ammonia can be used as the working fluid in the power cycle such as using the Kalina cycle.

## 3. Oxidation of contaminants in wastewater

Oxidation of hazardous contaminants in recalcitrant wastewater at high  $P_s$  and  $T_s$  is a known technology [9,11,15]. Supercritical water is known to be a good solvent for materials and a good medium for chemical reactions [11]. Wastewater can be pumped to the required  $P$  and contacted with air or O<sub>2</sub> to absorb enough O<sub>2</sub> to oxidize the contaminants and then injected in the geothermal reservoir. Solubility of O<sub>2</sub> in fresh water at 25 °C is ~207, mg/L at 25 bar and increases at the rate of 8.27 mg/L for each 1 bar increase in  $P$ . Oxygen can also be added as liquid H<sub>2</sub>O<sub>2</sub> at ambient  $T$  and  $P$ . As the water travels down the injection pipe its  $P$  and  $T$  increase at the rate of ~96 bar and <10 °C per 1 km of depth. This will keep the O<sub>2</sub> in solution. The water is treated as its  $T$  and  $P$  increase and the treated water which carries the heat from the EGS and the heat generated by the oxidation reaction exits the production well in the supercritical state. The oxidation process converts the organic carbon in the contaminants to CO<sub>2</sub>, the H<sub>2</sub> to H<sub>2</sub>O and the halogens to acids such as HCl. After neutralizing the HCl, the supercritical water can be used to drive the turbines of the power plant. This process conserves water because the treated water can be used in the power plant and then can be used for other applications after it is analyzed for residual hazardous materials.

## 4. Production of H<sub>2</sub> via steam reforming of CH<sub>3</sub>OH

Methanol is synthesized by reacting H<sub>2</sub> and CO produced by steam reforming of CH<sub>4</sub>. The EGS  $T_s$  are low for steam reforming CH<sub>4</sub>. The reforming reaction ( $\text{CH}_3\text{OH}(\text{liq}) + \text{H}_2\text{O}(\text{liq}) + \text{Heat} \leftrightarrow \text{CO}_2(\text{gas}) + 3\text{H}_2(\text{gas})$ ) can be used for capturing and transporting the EGS heat while producing H<sub>2</sub> [1,12,13]. The standard enthalpy of the reaction is about 130,000 kJ/kmol of CH<sub>3</sub>OH – over 2.5 times the heat that water can capture when it boils. This reaction can occur at  $T_s$  as low as 200 °C using catalysts [13]. Fig. 3 shows the equilibrium composition for the reforming reaction for a CH<sub>3</sub>OH/H<sub>2</sub>O mole ratio of 1:2. A liquid mixture of CH<sub>3</sub>OH/H<sub>2</sub>O can be injected into the EGS at room  $T$  and  $P$ . The products exiting the

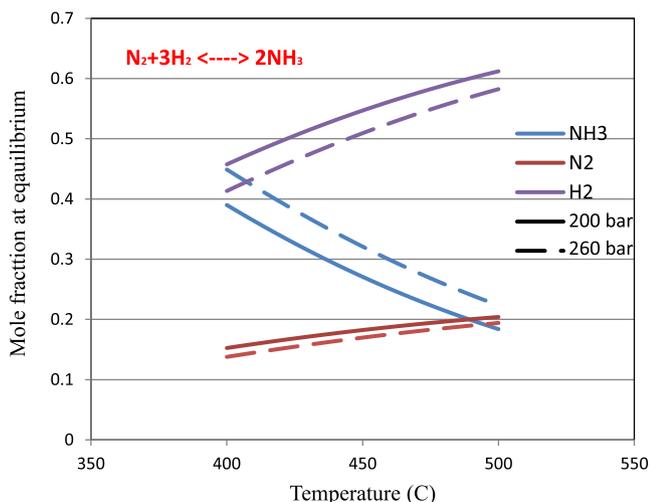


Fig. 1. Equilibrium composition of NH<sub>3</sub>, N<sub>2</sub> and H<sub>2</sub> at different temperatures and pressures.

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