

# UT-3 Hydrogen Separation Process Mass Flow Rate Characterization and Selection of Zirconium Silica Hydrogen Separator Membrane

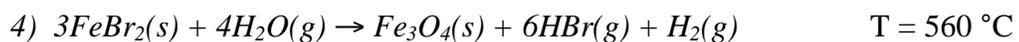
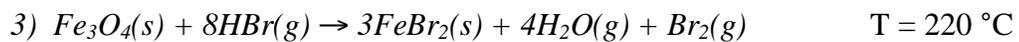
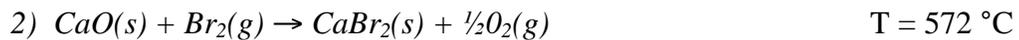
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## Abstract

The thermochemical UT-3 cycle has been chosen as the optimal method to produce 0.1 kg/s of H<sub>2</sub> to an adjoining bio fuels production plant. The chemical reactions and mechanicals of the process are outlined. A quantitative analysis of the mass flow rates in each leg, as well as the energy required by each heat exchanger, is conducted resulting in an initial characterization of the UT-3 cycle. Furthermore, a comparison of Hydrogen separation membranes is completed, identifying the ceramic Zr Silica membrane as the optimal choice. Future work is identified and briefly discussed.

## 1. UT-3 Process Overview

The thermochemical UT-3 Process utilizes the hydrolysis and bromination of solid Ca and Fe compounds to extract H<sub>2</sub> and O<sub>2</sub> from gaseous H<sub>2</sub>O entering the system using heat from a nuclear system [2]. The cycle consists of two Ca reactions and two Fe reactions occurring in four distinct reactors:



The steam is used to both react with solid chemicals to produce the desired products and mix with and transport gaseous products to the next reactor [6]. Once the reactions have run to completion in a forward progression, the flow of the steam cycle will be reversed, utilizing the products remaining in the reactors as the reactants for the corresponding reverse reaction. Figure 1 depicts a schematic of the UT-3 plant in forward flow. Heat exchangers (denoted by the orange, crossed circles) are placed in between the reactors to

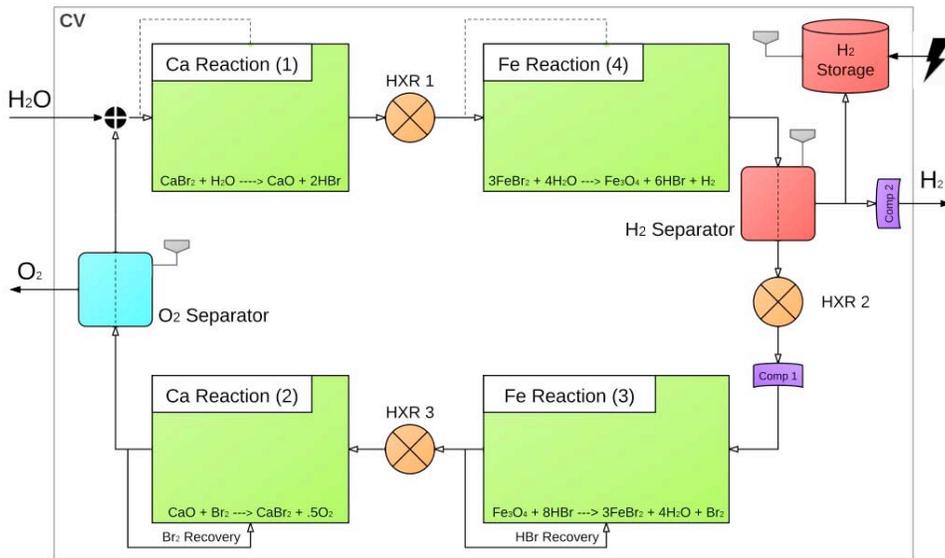


Figure 1: A schematic of the UT-3 cycle in forward progression.

flow) are placed in series with the reactors, creating the pressure differential to sustain the flow progression of the gaseous products [6].  $H_2$  and  $O_2$  separators remove the products from the system; the  $H_2$  will be sent to a bio fuels production plant while the excess  $O_2$  will be stored (its final use is currently undecided).

## 2. Mass Flow Rate Quantification

As the UT-3 cycle requires rigorous, time-dependent chemistry, three assumptions were identified to begin making mass flow rate calculations:

*First: All reactions progress to completion.*

Figure 2 depicts a block schematic of the compound flowing through each leg of the cycle in the forward progression. Applying this first assumption, the  $H_2O$  is completely consumed in the second reactor leaving  $HBr$  and the  $H_2$  to comprise the mass flow rate through the  $H_2$  separator leg. Furthermore, the  $HBr$  and  $Br_2$  recovery systems were ignored since the reactants will be completely consumed in reactors three and four. These modifications to the flow compounds are depicted in Figure 3.

ensure that the gaseous reactants enter the reactor at the correct temperature. Two compressors (one for forward flow, one for backward



Second:  $H_2$  must be transported to the bio fuels plant at a rate of  $0.1 \text{ kg/s}$  with a pressure of  $0.4 \text{ MPa}$  and temperature of  $25^\circ\text{C}$ .

This constraint imposed upon the UT-3 system allowed for a molar calculation of the Fe reactor (4). The molar values of products and reactants were propagated backward to Ca reactor (1), as well as forward to Fe reactor (3), Ca reactor (2), and ultimately through the  $O_2$  separator. This round of calculations represents the first iteration of the UT-3 cycle, with the resulting numbers depicted in Figure 4.

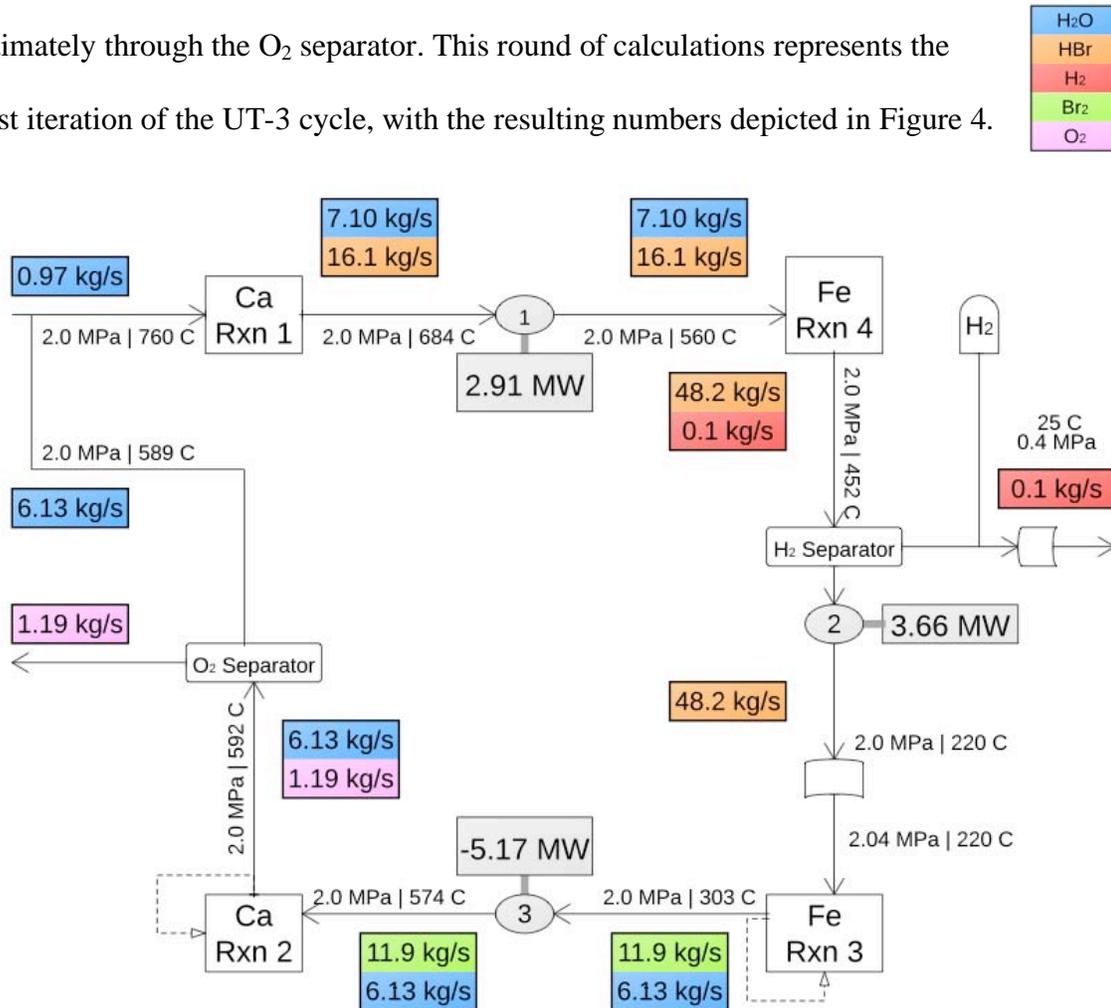


Figure 4: A block diagram of the forward flow for a UT-3 cycle producing  $0.1 \text{ kg/s}$  of  $H_2$  (assuming that all reactions go to completion).

Three: The reactors are optimized at temperatures  $760^\circ\text{C}$ ,  $57^\circ\text{C}$ ,  $220^\circ\text{C}$ , and  $560^\circ\text{C}$  [3].

Advanced chemical simulations have been applied to the reactions occurring in the UT-3 cycle, obtaining the optimal temperatures at which each reactor must be maintained [3]. From these values, the energy required by the system at each heat

exchanger could be characterized. These values appear as part of the schematic in Figure 4. At heat exchangers 1 and 2, the temperature of the gaseous mixture is lowered resulting in energy leaving the system at 2.91 MW and 3.66 MW respectively.

Conversely, heat must be applied to the gaseous products at heart exchanger 3, requiring 5.17 MW of energy into the system (i.e. -5.17 MW).

### 3. Hydrogen Membrane Separator Selection

Hydrogen membrane separation technology has emerged as an attractive option to the energy-intensive processes of cryogenic distillation and pressure swing adsorption [2], and consequently has been chosen as the method of H<sub>2</sub> separation for the UT-3 cycle. Various types of membranes exist, each offering benefits when optimized for the system's temperature. Of these choices, metallic membranes (optimized at ~350 °C) and ceramic membranes (optimized at ~500 °C) were identified as contenders. Ceramic

Table 1. Comparison of CVD (TEOS) and Zr Silica ceramic membranes

	<b>CVD (TEOS)</b>	<b>Zr silica</b>
<b>Diffusion</b>	<b>Solution-diffusion</b>	<b>Solution-diffusion</b>
<b>Permeance</b> [mol m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> ]	4.0 x 10 <sup>-8</sup> <i>(stated)</i>	10.0 x 10 <sup>-8</sup> <i>(extrapolated from fig. 6)</i>
<b>Pressure</b>	<b>2.0 MPa</b>	<b>2.0 MPa</b>
<b>Area Needed [m<sup>2</sup>]</b>	<b>1240</b>	<b>496</b>
<b>Concerns?</b>	Stability issues: phase transition  Poisoning issues: H <sub>2</sub> S, HCl, Co	Stability issues: phase transition  Poisoning issues: H <sub>2</sub> S, HCl, Co

membranes were ultimately chosen as they presented fewer poisoning concerns [2]. Looking at the permeance of the various types of ceramic membranes, a Zr Silica [4] membrane was compared

to the chemical vapor deposition tetra-ethyl-ortho-silicate (CVD TEOS)[5]. The results of the comparison are summarized by Table 1. The Zr silica was chosen specifically because it would require 496 m<sup>2</sup> of membrane area to achieve the 0.1 kg/s compared to the CVD TEOS which required 1240 m<sup>2</sup>.

#### 4. Future Objectives

The most critical step in the design of the UT-3 Hydrogen production plant will be a more rigorous analysis of the chemical system. First and foremost, the assumption that all chemical reactions progress to 100% completion must be relaxed, resulting in changing required reactant masses and consumption rates of those reactants. Relating to this relaxed assumption, the Br<sub>2</sub> and HBr recover systems in the two reactors before the H<sub>2</sub> separator must be both defined and characterized with respect to chemical separation, temperature requirements, and mass flow rates. At this time, an accurate characterization can be made of the time required by each reactor to near completion, allowing for a calculation of the optimal time for the flow switch.

The system may also benefit from an optimization of energy into and out of the system at the heat exchangers. With a total of 6.57 MW leaving the system and 5.17 entering the system, it may be possible to repurpose the energy out into heating the reactants in heat exchanger three. However, attention must be paid to the cost-benefit of implementing this system, as it may prove to be more energy demanding than the initial configuration. Continuing on with the thermodynamics of the system, both compressors in the system still require an energy characterization.

Though the Zr Silica membrane has been identified as the optimal choice for the UT-3 cycle, a significant amount of engineering will still be required. The primary concern is that the separator will require an area of 496 m<sup>2</sup> (assuming 100% separation of H<sub>2</sub>) to achieve the required mass flow rate of 0.1 kg/s. One option to explore is an increase in the pressure of the gaseous mixer in the H<sub>2</sub> separator, resulting in a reduced membrane area. Though there are no obvious drawbacks to this approach, the task will be thoroughly evaluated to provide the system with the optimal configuration.

## 5. References

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