The Temperature Dependence Analysis of Carbon Monoxide Conversion on CuO Bed of RDE Helium Purification System

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Abstract. RDE is an experimental power reactor that designed base on HTGR technology. This reactor has an indirect cycle power conversion system with primary coolant is helium and it secondary is water. RDE uses pebble fuel and multi-pass refuelling scheme. Helium coolant was predicted to be contaminated with various of gas impurities such as CO₂, H₂O, O₂, CH₄, N₂, and H₂ and CO. Those impurities must be maintained at certain limits by using Helium Purification System (HPS). Carbon monoxide (CO) is difficult to separate from the helium due to its small molecular size. Firstly, in HPS CO must be converted to CO₂ by using cupric oxide (CuO) in the CuO Column bed and then CO₂ will be adsorbed by molecular sieve. The CuO column bed operation temperature has a significant contribution to CO oxidation results. The purpose of this research was to determine the influence of temperature to oxidation process on CuO bed. The ChemCAD computer code modelling and simulation was used as a method. CuO bed is simulated by kinetic reactor and activation energy of each reaction is set up. The inlet mass flow rate of helium to CuO bed is 10.5 kg/h, 30 bar of pressure and the temperature has been varied to get the optimum result of CO₂. The simulation has shown that CuO bed optimum temperature for producing CO₂ is 250ºC. In the HPS, this temperature can be maintained by using heater that has been installed before CuO bed.

1. Introduction

Batan has responsibility to promote nuclear technology and now is designing Reaktor Daya Eksperimental which called RDE. The conceptual design of RDE is based HTGR [1]. This reactor has an indirect cycle power conversion system, helium as primary coolant and water as secondary. RDE uses pebble fuel and multi-pass refuelling scheme [2]. Except for electricity generation, RDE is also designed for cogeneration purposes as heat supporting for desalination, hydrogen production, coal liquefaction/gasification etc. Helium coolant was predicted to be contaminated with various of gas impurities such as CO₂, H₂O, O₂, CH₄, N₂, and H₂ and CO [3]. Those impurities must be removed and controlled below at certain limits by using Helium Purification System (HPS) [4], [5].

Base on HTGR operational experiences in the world, successful operation can be achieved by maintaining of high purity of helium in primary coolant [6]. Helium is chemically inert and it is thermally stable at high temperatures and under irradiation conditions. It does not easily interact with any substances [7]. Helium has a good characteristic and it can be used as a high thermal-dynamic substance and prospected to apply for primary coolant of RDE [8].
At beginning operation, helium impurities coolant are determined by chemical contaminants that presence in it. Those condition which take place in helium supplied from commercial suppliers [9]. Some impurities is released into helium during operation from any sources i.e. abrasion of fuel spheres, reactor components desorption, air residue and air/water in-leakage, fission products release from fuel, and water moisture from steam generator tube rupture/leakage, etc. [10].

HPS is responsible for maintaining the helium purity in primary coolant of RDE. The HPS and its auxiliary systems of RDE fulfill the following functions i.e. removes of gaseous, radionuclides and carbon dust contaminants from the primary coolant to maintain at a certain values, supplies purified helium to primary systems as helium make up system, removes of helium from the primary system and the helium filled supporting systems and storage in the purified gas store, relieving pressure and dumping helium from helium filled auxiliary and supporting systems and, possibly storing of radioactively contaminated helium. It can avoid graphite oxidation and corrosion of reactor structural materials like carburization and decarburization [11]. HPS will be an essential supporting system of RDE and set up to remove various impurities entering primary coolant maintain at specified levels [12]. These impurities are carbon dust and gas impurities such as H$_2$, H$_2$O, O$_2$, CO, CO$_2$, CH$_4$ and N$_2$ as well as krypton (K$_x$) and xenon (X$_x$) as some fission products [13]-[15]. HPS does not include a reactor safety related system [16], [17]. However, it is one of the most important auxiliary systems for RDE. Beside for purification purposes, it mitigated water ingress accident in primary coolant cause of steam generator tube ruptures (STGR) [18]–[22]. A few additional purification components for water ingress accident is needed and embedded in one train of HPS [3]. Those components are: filter, condenser, water separator with bigger size and volume.

HPS has four main components i.e. filter, CuO oxidizer bed, molecular sieve bed, and cryogenic carbon active[4]. Each of those units has their own pressure and temperature characteristics to optimize their function[23]. This paper analyses the CuO bed process function and reaction to find a good product on it. CuO bed is convert carbon monoxide to carbon dioxide by using CuO as oxidizer. The aim of the research is to get optimum temperature of CuO column bed. ChemCAD software was used to simulate kinetic reaction of CO and CuO. The temperature inlet of CuO bed is varied and carbon dioxide result is analyzed. The reactor unit operation in ChemCAD palette was used to simulate oxidation reaction

2. Methodology
The allowable values of gaseous impurities in primary coolant of RDE for normal operation are shown in Table 1. Carbon dusts particulates in primary coolant are low as possible and do not list in it. Comparing to HTGR experiences such as Dragon, Peach Bottom, AVR and HTR-10, this value is lower than set in those all HTGR plants. [15], [24]–[28]. Primary helium coolant mass flow rate is 4.3 kg/s, with total number of helium mass in the coolant is 210 kg. The mass flow rate value is determined by a purification constant, which shows helium mass fraction has been purified per hour. HPS bypass flow (as seen in Figure 1) in normal operation is approximately 10.5 kg/h, or hourly ratio of extracted helium gas to helium inventory in primary circuit is about 5%, equivalent to a purification constant of 0.05 h$^{-1}$. The purification constant rate for the AVR experimental reactor is 0.04 h$^{-1}$, HTR 10 is 0.05 h$^{-1}$ and the THTR-300 prototype reactor is 0.06 h$^{-1}$ [29]–[31].

| Impurities | H$_2$ | CO | N$_2$ | H$_2$ | CH$_4$ | O$_2$ | CO$_2$ |
|------------|------|----|-------|------|-------|------|-------|
| Limit value (vpm) | ≤ 0.2 | ≤ 3 | ≤ 1 | ≤ 5 | ≤ 1 | ≤ 0.02 | ≤ 0.6 |

*vpm = volume per million

Determination of the purification rate is very important in the design of HPS. If the flow rate is very large, a large enough HPS size is needed for the purification process to be effective. The large size of the HPS will increase RDE construction costs. If HPS is made in small size with low construction cost but inefficient of purification will have an impact on the safety of RDE operations.

The worldwide practical experiences in helium purification showed that contaminants are removed from helium by chemical reactions, filtration, and adsorption [13], [15], [30], [32]–[35]. Carbon dust and fission products release to the coolant are removed by mechanical filters. As a result
of chemical reaction with copper oxide (CuO), contaminants of hard-sorbed gases impurities (hydrogen and carbon monoxide) are chemically converted into easy-sorbed water and carbon dioxide. Then these impurities are removed from helium by zeolitic adsorbers or molecular sieve. Activated carbon cooled by liquid nitrogen is used to remove nitrogen, xenon, krypton, methane and oxygen. Filters are replaced after saturated condition is achieved by pressure differences or radiation exposure parameter. CuO oxidizer is regenerated by using oxygen injection to reactor column bed. Adsorbers is isolated and regenerated by pressure release and increasing temperature.

![Figure 1. Process Flow Diagram (PFD) of Helium Purification System of RDE [5]](image)

The CuO bed in HPS is modeled by using ChemCAD as shown in Figure 2. The stream no. 1 is helium plus CO and stream no. 2 is CuO. The output stream (stream no. 3) is CO₂. Helium mass flow rate is 10.2 kg per hour with concentration of CO is 10 gram per hour. CuO as oxidizer in 0.001 kg per hour of mass flow rate enter to the reactor bed. CuO is not available in ChemCAD database material and its properties must add in database as seen in Table 2. Kinetic reaction parameters of conversion reaction are seen in Table 3.

### Table 2. Carbon monoxide material properties

| Parameter                   | Value                                                                 |
|-----------------------------|-----------------------------------------------------------------------|
| Molecular formula           | CO                                                                   |
| Molar mass (g/mol)          | 28.0101                                                             |
| Specific                    | Odourless and colourless                                              |
| Density (g/cm³, liquid)     | 0.789                                                                |
|                             | 1.250 g/L at 0 °C, 1 atm                                             |
|                             | 1.145 g/L at 25 °C, 1 atm                                            |
| Melting point               | 68 K, (-205 °C)                                                      |
| Boiling point               | 81 K (-192 °C)                                                       |
| Solubility in water         | 0.0026 g/100 mL (20 °C)                                              |
| Dipole moment               | 0.112 D (3.74×10⁻³¹ C·m)                                             |
Figure 2. The CuO kinetics reactor bed

Table 3. Oxidation kinetics reaction data of hydrogen and carbon monoxide

| Parameter          | Oxidation of H₂ + CuO | Oxidation of CO + CuO |
|--------------------|-----------------------|-----------------------|
| Pressure           | 1 atm                 | 1 atm                 |
| Temperature        | 473 °K                | 773 °K                |
| Activation energy (Ea) | 14.5 kkal/mol         | 20 KJ/mol             |
| Reaction rate constant (k) | 3.4656 x 10⁻²      | 30.9656               |
| Reaction order     | 1                     | 0.7                   |

3. Result and discussion
The oxidation reaction of CO by oxidizing CuO in the helium coolant purification system of RDE is as follows:

\[ \text{CO} + \text{CuO} \xleftarrow{v_1 \times 2} \text{CuO(CO)} \xleftarrow{v_3 \times 4} \text{Cu} + \text{CO}_2 \]

Where: \( v_1 \) is reaction rate of CO and CuO, \( v_2 \) is reaction rate from CuO(CO) to CO and CuO, \( v_3 \) is reaction rate of CuO(CO) into CO₂ and Cu, \( v_4 \) is reaction rate Cu and CO₂ to be CuO(CO). Oxidation of CO and CuO indirectly produces CO₂ and Cu, through intermediate species CuO(CO). The amount of CO which can be oxidized to CO₂ relies heavily on the equilibrium reaction rate \( v_1 \) and \( v_2 \) and \( v_3 \) and \( v_4 \) where these conditions rely heavily against temperature oxidation reactions are given.

Simulation results of CO oxidation by CuO are shown in Figure 3. It can be seen that increasing in oxidation temperature from 200 °C to 350 °C resulted also in increasing of oxidation reactions rate. It is indicated by reactant (CO) reduction from 110 g/hour to 4 g/hour of mass flow rate which means that CO must react of 3.785 moles per hour, but the CO₂ product produced is only 1.136 moles per hour. In accordance with oxidation stoichiometry if all CO is converted to CO₂, total number of CO₂ produced must be 3.785 moles per hour.

It means only 30% of CO has been converted to CO₂ and the rest of 70% is still in intermediate condition of CuO(CO) and total amount of CuO(CO) is 2.679 moles per hour. CuO(CO) is in solid properties during reaction process. It has benefit not to release to the helium flow and it does not disturb the next adsorption phase.

In temperature of 160-340°C shows CO₂ production increase from 56 gram per hour to 259 gram per hour and CuO(CO) remaining always decreases. This means that the oxidation reaction to convert CO to CO₂ is still quite effective. At temperature of 245 °C and between 280 °C to 340 °C there is a shift in equilibrium in which Cu and CO₂ as the oxidation reaction product reacts to produce
CO again so that the perfect conversion target of CO is not achieved. This can happen because at that temperature the reaction rate of \( v_2 \) is greater than \( v_1 \) and \( v_4 \) is also greater than \( v_3 \).

At the next temperature rise which is 300 °C to 340 °C the oxidation reaction stops completely, meaning that no reaction product produced by CO reactants is still constant of 0.173 kg/hr and CuO also remains of 45.0 kg/hr. It is possible that at this temperature condition Gibbs G free energy in the CO oxidation reaction with CuO is positive (greater than zero) so that the reaction is not spontaneous or stops.

CuO(CO) species as an intermediate plays an important role in the process of CO oxidation reaction by CuO where the product continues to increase to the most condition at the reaction temperature of 250 °C and the subsequent increase in temperature continues to decrease. In Figure 3, at a temperature of 250 °C the CuO(CO) curve looks close to flat. It is understood that at this temperature the CuO (CO) species is stable and does not form the next chain reaction. Because if there is a subsequent chain reaction it will have an impact on the increase in impurity gas. Thus it can be determined that at 250 °C temperature is the optimal temperature for the CO oxidation process by CuO. This is also supported by the flow rate of CO as reactant which has also reached 0.0 g/hour and CO\(_2\) products reach 133 g/hour.

The conceptual design of column oxidizer CO in the reactor coolant purification process besides based on optimal temperature 250 °C must also consider the energy utilization factor (EUF) which is also influenced by the mass flow rate in the helium inventory system when greater mass flow rate would decrease the EUF RGTT200K.

![Figure 3. Correlation between oxidation rate versus oxidation temperature in kinetic reaction of carbon monoxide oxidation](image)

Figure 3. Correlation between oxidation rate versus oxidation temperature in kinetic reaction of carbon monoxide oxidation

CuO column temperature must be maintained at 250 °C for oxidizing reaction runs optimally. Therefore to maintain it is stable at 250 °C, a heater is installed before column bed as seen in Figure 1. This heater works according to the temperature sensor signal inside the CuO column. If the column temperature is less than 250 °C, the heater will be turned on, and will turn off when the temperature reaches 250 °C.

Activation energy or \( E_a \) of a chemical reaction is the energy differences between reactants and activated complexes, it is known as transition states. This condition state is defined as the biggest energy state of the system. If the molecules or compound in the reactants collides with enough kinetic energy and this energy is bigger than the energy of the displacement/transition state, then the reaction occurs and the product is formed. The higher the activation energy, the harder the reaction occurs and
vice versa. In this simulation, the optimal temperature for the highest activation energy of the kinetic reaction is at 250 °C.

4. Conclusion
The effect of temperature on the CO oxidation by CuO in HPS has a significant impact on the formation of oxidation products i.e. CO₂, CuO (CO), and Cu. CO converted to CO₂ increase at higher temperature and vice versa. The optimum temperature of CO oxidation is achieved at 250 °C. The CO oxidation column operation must be designed at 250 °C by considering mass flow rate effect on HPS inlet.

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