THE ADSORBER COMPONENT ADDITION IN CHEMCAD SOFTWARE PALETTE FOR HELIUM PURIFICATION MODELLING AND SIMULATION

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ABSTRAK


Kata kunci : penambahan, komponen adsorber, ChemCAD, pengotor, purifikasi, RDE

ABSTRAK

THE ADSORBER COMPONENT ADDITION IN CHEMCAD SOFTWARE FOR HELIUM PURIFICATION MODELLING AND SIMULATION. Helium purification system (HPS) is an important system in RDE. This system removed dust particles and gas impurities in primary coolant of RDE. The impurities are dust carbon, N₂, O₂, H₂, O₃, CH₄, CO, and CO₂. One of the components which required in HPS is an adsorber. In ChemCAD software palette, adsorber component is not yet available and should be added. This paper discussed the adsorber component addition in ChemCAD. The addition is made by using Excel icon facility, while coding is made by using Visual Basic. The purpose of adding adsorber component to ChemCAD palette is it can be used for helium purification modeling. The adsorption process principle used in adsorber modeling is Langmuir method. After finishing the coding, adsorber component will be integrated into ChemCAD. This component then used for modeling and simulated the helium purification of primary coolant of RDE especially for oxygen adsorption. The simulation results are compared to SuperPro Designer modeled which is also demonstrated the same problem. The differences results of adsorber component simulation between ChemCAD and SuperPro Designer did not more than 0.02%. It can be concluded that the adsorber component which is added to the ChemCAD is valid so it can be used to simulate the helium purification system in RDE.

Keywords : adsorber component, addition, ChemCAD, impurities, RDE.
1. INTRODUCTION

Reaktor Daya Eksperimental (RDE) is developed in BATAN. This reactor is designed based on HTGR technology\([1]\). RDE has indirect cycle power conversion system and uses pebble fuel type. The primary coolant of RDE is helium and secondary is water. Helium purification system (HPS) is an important system in RDE. This system removes impurities contained in primary helium cooling system\([2,3]\). There are two kinds of impurities i.e. particulates and gaseous form\([4]\). The particulates impurities are graphite dust and fission products releases from the reactor core, and the gaseous impurities are \(\text{N}_2, \text{O}_2, \text{H}_2, \text{O}_2, \text{CH}_4, \text{CO, H}_2\text{O and CO}_2\)\([5]\). Based on HTGR operating experiences graphite dust is very small, but it must be cleaned from the reactor coolant due to negative impact to system, structure and component (SCC) of reactor. The carbon dust will adhere to SCC reduces heat removal capacity\([6,7]\). Carbon dust is generally derived from the pebble fuel friction in the core. The gaseous impurities are derived from the interaction between water/air ingress with fuel/reflector\([2]\).

ChemCAD (Chemical Computer Aided Design) is a software that can be used for process modeling in various industries\([8]\). This software will be used to simulate the helium purification system of RDE. HPS has several main components including cyclone separator, filter, chemical reactors, condenser, and adsorber\([9]\). Cyclone and filter used to remove carbon dust and other particulates impurities. Chemical reactors used to simulate the CuO oxidizer column bed. CuO is a catalyst in converting molecules of CO to \(\text{CO}_2\) also converting \(\text{CH}_4\) and \(\text{H}_2\) into \(\text{CO}_2\) and \(\text{H}_2\text{O}\) respectively\([10]\). The \(\text{H}_2\text{O}\) output from column bed separated by water trap and \(\text{CO}_2\) is captured by the molecular sieve adsorber. Other impurities gases such as \(\text{N}_2\) and \(\text{O}_2\) will be adsorbed in the last stage of activated carbon. The \(\text{N}_2\) and \(\text{O}_2\) molecular size is very small to capture them it required cryogenic conditions in the temperature of -180 °C\([11,12]\).

Two important components in the HPS are molecular sieve and activated carbon adsorber\([13]\). In process modeling usually adsorber component is used to simulate them. Both of these components are not available in ChemCAD therefore it must be created to simulate the HPS. This paper discusses the built of adsorber components to ChemCAD palette and integrate it into the HPS system. The purpose of creating adsorber component is to simulate the HPS in RDE. At first, adsorber coding is made based on Langmuir method by using Visual Basic. After this coding finished, it will integrated into ChemCAD with Excel icon facility in its palette. The component addition in ChemCAD will be validated and compared by using SuperPro Designer computer code with the same case of adsorption process in HPS. The comparing results expected very low differences between of both simulation executions so the adsorber component in ChemCAD can be used for HPS simulation.

2. THEORY

2.1 The Langmuir Adsorption in Isothermal Condition.

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface\([8]\). This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the absorbate) is dissolved by or permeates a liquid or solid (the absorbent), respectively\([14]\). Adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it. Adsorption is a surface phenomenon.

Adsorption capacity is the ability of an adsorbent attracts a number of adsorbate. The adsorption process depends on, among others: a specific area of solids (adsorbent surface area), the concentration of solute or pressure equilibrium gas adsorption, the temperature during the process and the nature of the adsorbate or adsorbent itself.
greater the surface area of the adsorbent, the adsorption power will grow stronger. Adsorption on the surface properties of solids are highly selective means that the mixture of substances is only one component adsorbed by certain solids. By its nature, there are two types of adsorption i.e. physical and chemical adsorption. Differences between both types are shown in Table 1. There are some methods in adsorption process i.e. Henry method, the Freundlich method and Langmuir method.

Table 1. The differences between chemisorption and physisorption\cite{11}.

<table>
<thead>
<tr>
<th>Physically adsorption (physisorption)</th>
<th>Chemically adsorption (chemisorption)</th>
</tr>
</thead>
<tbody>
<tr>
<td>It arises due to van der Waals forces</td>
<td>It arises due to chemical bond formation</td>
</tr>
<tr>
<td>Enthalpy of adsorption is low (20-40 kJ/mol)</td>
<td>Enthalpy of adsorption is high (80-240 kJ/mol)</td>
</tr>
<tr>
<td>It is reversible</td>
<td>It is irreversible</td>
</tr>
<tr>
<td>It is not specific in nature</td>
<td>It is highly specific in nature</td>
</tr>
<tr>
<td>No appreciable activation energy is required</td>
<td>High activation energy is sometimes required</td>
</tr>
<tr>
<td>It depends on the nature of the gas. More easily liquefiable gases are adsorbed reactly</td>
<td>It also depends on the nature of the gas. Gases which can react with the adsorbent, show chemisorption</td>
</tr>
</tbody>
</table>

2.2 Adsorber Unit and Adsorption Process Modeling

Unit operation (component) adsorber can be used to simulate the process of adsorption on a molecular sieve and activated carbon. The mass transfer process of adsorbate gas to the adsorbent using equation (1), and the solid-gas equilibrium described by Henry balance equation (2), Freundlich equation (3) and Langmuir equations in isothermal (4).

\[
F_A = k_y a \frac{\rho_y}{M_r} \left(y_A - y_A^*\right) S \Delta z \varepsilon \hspace{1cm} (1)
\]

\[
y_A^* = H_A x_A \hspace{1cm} (2)
\]

\[
y_A^* = K_f x_A^n \hspace{1cm} (3)
\]

\[
y_A^* = \frac{a x_A}{1 + bx_A} \hspace{1cm} (4)
\]

where \( F_A \) is the adsorbate mole transferred to the adsorbent per time (mol/s), \( k_y \) is the mass transfer coefficient in the gas phase (m²/s), \( a \) is the area per unit volume (m²/m³), \( y_A \) is the mole fraction of adsorbate in gas, \( y_A^* \) is the adsorbent mole fraction on the surface of the adsorbent, \( S \) is the cross-sectional area of the column (m²), \( \Delta z \) is the length increment (m), \( \varepsilon \) is the porosity of the bed, \( H_A \) is the Henry constant, \( K_f \) and \( n_f \) is the Freundlich equilibrium constant, \( A \) and \( b \) are Langmuir equilibrium constants, \( x_A \) is the adsorbate mole fraction per mass of adsorbent.

2.3 Mass balance adsorbate in the adsorption process increment of volume S.\( \Delta z \)

In the adsorption process of adsorber having an adsorbent of S volume, with increment of \( z + \Delta z \), can be solved by equation of (5), (6) and (7). The volume adjustment model of adsorber is shown in Figure 1.

Figure 1. The increment model of adsorber volume.
Mass flow rate of input – mass flow rate of output – adsorption rate = rate of gas accumulation ................................................................. (5)

\[
(G_{y_A}^{+} - G_{y_A}^{-}) + \left[ D_{cat} eS \frac{\rho_{g}}{M_{g}} \frac{\partial y_A}{\partial t} \right]_{t=\Delta t} - \left[ D_{cat} eS \frac{\rho_{g}}{M_{g}} \frac{\partial y_A}{\partial t} \right]_{t=\Delta t} - k_{s}(y_A - y_A^{+})a \frac{\rho_{g}}{M_{g}} S \Delta \varepsilon = S \Delta \varepsilon \frac{\rho_{g}}{M_{g}} \frac{\partial y_A}{\partial t}
\]

2.4 Mass balance adsorbate in the solid volume element

\[
k_{s}(y_A - y_A^{+})aS \Delta \varepsilon \frac{\rho_{g}}{M_{g}} - 0 = S \Delta \varepsilon (1 - \varepsilon) \rho_{p} \frac{\partial x_A}{\partial t}
\]

Where the initial condition of \( x_A (z, 0) = 0 \), \( y_A (z, 0) = 0 \), and boundary condition of \( y_A (0, t) = y_{Ain} \). The value of \( G \) is the mass flow rate or \( G = \text{mol flow (gmol/s)} \), and \( \rho_{b} = \text{bulk density (g/m3)} \). Determination of the physical parameter of the Diffusivity property \( (D_m) \) can be determined by equation (8). (Coulson and Richardson, 1983)

\[
D_m = 1.10^{-7} T^{1.75} \left( \frac{BM_{H_2} + BM_{CO_2}}{BM_{H_2}BM_{CO_2}} \right)^{1/2} \frac{P}{101325 \left( u_{H_2}^{1/3} + u_{CO_2}^{1/3} \right)^2}
\]

Where \( BM_{i} \) is the molecular weight (g/gmol), the \( u_{i} \) is the diffusion volume. The axial dispersion coefficient value is shown in equation (9).

\[
D_{cat} = 0.37D_m + \frac{0.5v_{sp} d_p}{1 + \frac{9.7D_m}{v_{sp} d_p}}
\]

Where \( v_{sp} \) is superficial velocity, the mass transfer coefficient is calculated using equation (10) and the Reynold number in equation (11)

\[
k_{y} = \frac{D_m}{d_p} (2 + 1.1 \text{Re}^{0.6} \text{Sc}^{1/3})
\]

\[
\text{Re} = \frac{d_p v_{sp}}{v}
\]

\[
\text{Sc} = \frac{\mu}{D_m}
\]

where \( d_p \) is the particle diameter (m), \( v \) is the superficial velocity (m/s), kinematics viscosity (m²/s), and \( \mu \) is the viscosity (Pa.s). To calculate cross...
sectional area is using the equation: \( S = \pi R^2 \), with \( R \) = radius of bed (m), specific surface specification calculated by equation (13) and superficial velocity equation calculated by equation (14).

\[
a = \frac{6(1-\varepsilon)}{d} \\
v_s = \frac{G}{\frac{\rho_g}{M_r} S}
\]

Where \( G \) is mass flow rate or mol flow (gmol/s), with the equilibrium constant is determined by literature or experimental research.

3. METHODOLOGY

The existing of components in ChemCAD palette has its limitations. The adsorber component did not available in palette. However, in ChemCAD software there is an Excel icon feature to make some components addition. With this feature, we can create program coding of component with its function by using Visual Basic and add it as a new component in ChemCAD palette. The icon of the Excel unit operation in the ChemCAD palette is shown in Figure 2. In this study the adsorber component will be added, the adsorber component will be used to model the molecular sieve and activated carbon in the HPS of RDE. Both of these components conduct to adsorbed the helium gas impurities i.e. CO, H\(_2\)O, CO\(_2\), N\(_2\) and O\(_2\).

![Figure 2. Icon Excel of Unit operation in ChemCAD.](image)

Table 2. The input value for adsorber modeled and simulation

<table>
<thead>
<tr>
<th>Helium mass flow rate</th>
<th>: 10.5 kg/hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium temperature</td>
<td>: -180 C</td>
</tr>
<tr>
<td>Helium pressure</td>
<td>: 30 bar</td>
</tr>
<tr>
<td>Oxygen concentration (as impurity)</td>
<td>: 10</td>
</tr>
</tbody>
</table>
Figure 3. The flowchart for the adsorber coding in Langmuir method.

The main primary coolant stream of RDE is 4.3 kg per second, and the HPS bypass flow rate is designed of 5% or about 0.215 kg per second. The RDE parameters used in this model are shown in Table 2. The results from the ChemCAD is compared with SuperPro Designer adsorber model which is shown in Figure 4 and Figure 5.
4. RESULT AND DISCUSSION

The adsorber component has already integrated with the ChemCAD and used to create an HPS model of RDE especially for adsorption process. Simulation is done to validate the adsorber process function. The results from the ChemCAD is compared with SuperPro Designer adsorber model. Both of this software is built for industrial process modeling. In SuperPro, there are three optional mode choice for gas adsorption. First is Langmuir, second is Henry and the third is Freundlich method. Adsorption modeling in ChemCAD is used Langmuir method so it can be compare by using SuperPro by choosing the same method (first mode option).

The last stage of HPS is the adsorption of N\(_2\) and O\(_2\) uses activated carbon. This process operates at very low temperatures (cryogenic), i.e. -180 °C. In HPS train, the outside carbon column is circulated by liquid nitrogen to maintain very low temperature. The N\(_2\) and O\(_2\) gases will be adsorbed into the activated carbon, when reached it saturation the activated carbon will be regenerated. One of the specifications of activated carbon used as shown in Table 3.
Table 3. Active carbon specifications in cryogenic condition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value/unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spesific volume</td>
<td>0.6 cm³/g</td>
</tr>
<tr>
<td>Average porosity diameter</td>
<td>24 Å</td>
</tr>
<tr>
<td>Particle size</td>
<td>2 mm or 5 mm</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>1100 m²/g</td>
</tr>
<tr>
<td>Internal porosity</td>
<td>55% - 75%</td>
</tr>
<tr>
<td>Zeolithe density</td>
<td>450 kg/m³</td>
</tr>
</tbody>
</table>

The comparison results of simulation both of those two softwares are shown in Table 4.

Table 4. The effect of active carbon adsorption to the O₂ gas.

<table>
<thead>
<tr>
<th>Duration (hour)</th>
<th>O₂ remaining (ppm)</th>
<th>Duration (hour)</th>
<th>O₂ remaining (ppm)</th>
<th>Differences (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.0018</td>
<td>0.5</td>
<td>0.0019</td>
<td>5.2632</td>
</tr>
<tr>
<td>0.75</td>
<td>0.0022</td>
<td>0.75</td>
<td>0.0021</td>
<td>-4.7619</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0026</td>
<td>1.0</td>
<td>0.0025</td>
<td>-4.0000</td>
</tr>
<tr>
<td>2.0</td>
<td>0.0055</td>
<td>2.0</td>
<td>0.0054</td>
<td>-1.8519</td>
</tr>
<tr>
<td>3.0</td>
<td>0.0114</td>
<td>3.0</td>
<td>0.0115</td>
<td>0.8696</td>
</tr>
<tr>
<td>3.5</td>
<td>0.0164</td>
<td>3.5</td>
<td>0.0165</td>
<td>0.6061</td>
</tr>
<tr>
<td>4.0</td>
<td>0.0237</td>
<td>4.0</td>
<td>0.0238</td>
<td>0.4202</td>
</tr>
<tr>
<td>4.5</td>
<td>0.0342</td>
<td>4.5</td>
<td>0.0340</td>
<td>-0.5882</td>
</tr>
<tr>
<td>5.0</td>
<td>0.0494</td>
<td>5.0</td>
<td>0.0493</td>
<td>-0.2028</td>
</tr>
<tr>
<td>5.5</td>
<td>0.0712</td>
<td>5.5</td>
<td>0.0713</td>
<td>0.1403</td>
</tr>
<tr>
<td>6.0</td>
<td>0.1028</td>
<td>6.0</td>
<td>0.1029</td>
<td>0.0972</td>
</tr>
<tr>
<td>6.5</td>
<td>0.1483</td>
<td>6.5</td>
<td>0.1482</td>
<td>-0.0675</td>
</tr>
<tr>
<td>7.0</td>
<td>0.2139</td>
<td>7.0</td>
<td>0.2138</td>
<td>-0.0468</td>
</tr>
<tr>
<td>7.5</td>
<td>0.3088</td>
<td>7.5</td>
<td>0.3089</td>
<td>0.0324</td>
</tr>
<tr>
<td>8.0</td>
<td>0.4455</td>
<td>8.0</td>
<td>0.4454</td>
<td>-0.0225</td>
</tr>
<tr>
<td>8.5</td>
<td>0.6428</td>
<td>8.5</td>
<td>0.6429</td>
<td>0.0156</td>
</tr>
<tr>
<td>9.0</td>
<td>0.9275</td>
<td>9.0</td>
<td>0.9276</td>
<td>0.0108</td>
</tr>
<tr>
<td>9.5</td>
<td>1.3384</td>
<td>9.5</td>
<td>1.3382</td>
<td>-0.0149</td>
</tr>
<tr>
<td>10.0</td>
<td>1.9311</td>
<td>10.0</td>
<td>1.9313</td>
<td>0.0104</td>
</tr>
<tr>
<td>10.5</td>
<td>2.7862</td>
<td>10.5</td>
<td>2.7863</td>
<td>0.0036</td>
</tr>
<tr>
<td>11.0</td>
<td>4.0212</td>
<td>11.0</td>
<td>4.0214</td>
<td>0.0050</td>
</tr>
<tr>
<td>11.5</td>
<td>5.7969</td>
<td>11.5</td>
<td>5.7968</td>
<td>-0.0017</td>
</tr>
<tr>
<td>11.8</td>
<td>6.9710</td>
<td>11.8</td>
<td>6.9712</td>
<td>0.0029</td>
</tr>
<tr>
<td>11.8</td>
<td>7.1097</td>
<td>11.8</td>
<td>7.1098</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

The differences between SuperPro and ChemCAD simulation results is not more than 0.02%. The oxygen concentration adsorbed is shown in Figure 6. After going through the process of absorption with Activated Carbon is expected to have pure helium. The purified helium will be stored into storage tanks. Cryogenic conditions are conditions at very low temperatures. In this simulation the cryogenic condition that.
applied to the Activated Carbon is -180 °C of temperature. At that condition the absorption capacity of activated carbon becomes larger because the gas impurities moved more slow and it makes easier to be absorbed\[^{13}\].

Except temperature, the ability of active carbon adsorption to N\textsubscript{2} and O\textsubscript{2} impurities is determined by many factors, including contact time and the amount of activated carbons. Sufficient contact time allows the adsorbate to be adsorbed into the surface of the adsorbent, and less contact time results in not achieving the adsorption equilibrium so that impurities taken are not optimal. Therefore the active carbon bed is simulated with a height of 15 m, it is expected that the adsorbate has sufficient contact time to be absorbed by the adsorbent. In this study, to determine the time of regeneration of activated carbon is done by observing the concentration of impurities N\textsubscript{2} and O\textsubscript{2} on the clean output stream of activated carbon bed, i.e. stream number 3.

Based on the maximum limit of O\textsubscript{2} impurity gas allowed in helium coolant is 0.02 ppm\[^{14}\], if it is using the active carbon bed design as much as 654.16 kg as above bed design then after operating for 3.5 hours active carbon must be regenerated. From Table 2, it is known that at time of 3.5 hours, the remaining O\textsubscript{2} impurity concentration is 0.0164 ppm, and at time of 4 hours, the impurity concentration has exceeded 0.02 ppm.

The O\textsubscript{2} impurity conditions used in this simulation is 1018 ppm or equivalent to 50,900 times the normal operating conditions of RDE, so if it is implemented in HPS, and the RDE operates under normal conditions it can be concluded that the active carbon bed will be outage (3.5 x 50,900) hr = 178,150 hours or equivalent to 7422 days.

![Figure 6. The correlation between adsorption duration vs remaining O\textsubscript{2} in the output stream of carbon active column bed.](image)

5. CONCLUSION

One of the components which is required in HPS is an adsorber. At ChemCAD software, adsorber component is not yet available and should be added. The adsorption principle used in adsorber components is Langmuir method. The additions will used excel icon feature in ChemCAD palette, and the coding is created using by Visual Basic. After finishing the coding step, adsorber component integrated into ChemCAD. This component then used to modeled and simulated the helium gas purification of RDE. The simulation results are compared to SuperPro Designer which is also simulated the same problem. The results shown that ChemCAD and SuperPro
Designer differences did not more than 0.02%. It can be concluded that the adsorber component which is added to the ChemCAD software can be used to simulate the helium purification system in RDE reactors.

6. ACKNOWLEDGEMENT

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7. REFERENCES