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# **3D** Simulation of the Purification of Carbon Monoxide with CuCl(7.0)/AC by the Pressure Swing Adsorption Process

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# ABSTRACT

In this work, the separation of carbon monoxide (CO) from a synthesized gas (syngas) mixture was modeled. It was considered a copper-based adsorbent consisting of cuprous chloride (CuCl) on an activated carbon (AC) support (CuCl/AC) in a pressure swing adsorption (PSA) process. First, the adsorption of syngas components on the CuCl/AC adsorbent at 303.15 K was simulated to determine the required data. Next, the PSA process of separating CO from syngas using the CuCl/AC absorbent at ambient temperature and pressure of 1000 kPa was evaluated by the computational fluid dynamics simulation. The simulation results showed that with an adsorption bed of 2 m in height and 1 m in diameter, CO with appropriate purity (~ 99.5 %) was separated from syngas by CuCl/AC. In addition, reducing the inlet feed pressure, or in other words, its velocity or flow can increase the efficiency of the operation (e.g., with a shorter bed height of 0.5 m, a CO purity of more than 99.8 % can be achieved at 700 kPa, but with a significant increase in the operating cost).

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# 1. Introduction

Known as the silent killer, carbon monoxide (CO) is a colorless, odorless, tasteless and highly toxic gas produced by the incomplete combustion of fossil fuels. CO poisoning is the most common form of fatal poisoning in France and the United States [1]. Nevertheless, there are several large-scale industrial processes in which CO is the main source for producing more valuable compounds. The basic Fischer-Tropsch process for liquid fuel production is the most well-known example where CO is used. Another important process that requires pure CO is hydroformylation, in which it is used a homogeneous catalytic reaction to convert CO and alkenes to aldehydes. The aldehyde products can be further hydrogenated to produce alcohols that eventually become plasticizers and detergents [2]. CO is also used to produce methane (CH<sub>4</sub>), phosgene (COCl<sub>2</sub>), methanol (CH<sub>3</sub>OH), glycol  $(C_2H_6O_2)$ , acetic ethylene acid (CH<sub>3</sub>COOH), formic acid (CH<sub>2</sub>O<sub>2</sub>), propionic  $(C_{3}H_{6}O_{2}),$ acrylic acid acid  $(C_{3}H_{4}O_{2}),$ formaldehyde (CH<sub>2</sub>O), dimethylformamide  $(C_3H_7NO),$ oxalates, metal carbonyls, isocyanates, pesticides, herbicides, and raw materials for the production of polyurethane foams, polycarbonate plastics, etc. It has actual applications that turn this gas into an essential raw material in the chemical industry. In most of these processes, CO with a purity greater than 99 % is required, making the CO separation critical [3-6]. During the process of the separation and purification of CO, for example, from the synthesized gas (syngas) mixture, which is one of the most widely used cases, the impurity of the products such as CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O compounds must be removed. The cryogenic distillation, membrane separation, absorption and adsorption methods are frequently examined [7]. However, it isn't easy to separate components with similar physical properties using conventional distillation. For example, CO and N<sub>2</sub> have boiling points of 82 and 78 K. In addition, the molecular sizes of CO and N<sub>2</sub> are very close to each other, 3.67 and 3.64 Å respectively, which makes it very difficult to them through separate the membrane efficiently. As a result, developing an efficient process for the separation and purification of CO attracts much attention [8]. The CO separation through cryogenic distillation also deals with similar boiling points of the components. Some frequently used absorption processes use liquids such as ammoniacal cuprous chloride and aromatic solution with CuAlCl<sub>4</sub> as (COSORB) absorbers. They have drawbacks of the high energy consumption, high operating costs, and usually the addition of new impurities from liquid to gas. On the

contrary, adsorption processes, such as pressure swing adsorption (PSA), vacuum pressure swing adsorption (VPSA) and temperature swing adsorption (TSA) benefit from the lower energy consumption, moderate costs and easy operation. Porous materials such as zeolites, activated carbon (AC) and metal-organic frameworks (MOFs) can be used in adsorption. Due to the need to regenerate adsorbents in the most commercial applications, the adsorption processes are carried out cyclically, where the pressure conservation is of great importance [5, 9]. Since the available feed gas (a mixture containing CO, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub>) has a pressure of about 1000 kPa and a temperature of about 303 K, the CO separation by the adsorption process with minimal changes in pressure and temperature (outlet to inlet) simultaneously with the shortest process time, i.e. PSA, is the most suitable process.

For adsorption-based separations, adsorbents are vital in determining the separation performance. Porous materials, including AC, activated alumina, zeolites and MOFs, can adsorb CO. However, they suffer from low adsorption capacity and low selectivity. They have been modified with Cu(I) to form complex adsorbents capable of forming  $\pi$ bonds between CO and Cu(I) ions, which are stronger than van der Waals forces. This leads to high adsorption capacity and selectivity. In addition, their adsorption performance can be improved by breaking these  $\pi$  bonds using simple engineering operations such increasing the temperature or decreasing the pressure. In this case, Cu(I)-based ACsupported adsorbents are very useful due to their excellent versatility, no need for detoxification, and low cost [8, 10].

Gao et al. [11] studied the synthesized ACsupported CuCl (CuCl/AC) for CO adsorption and demonstrated that with only the copper loading of 7 mmol/g AC, the sorbent has a high CO adsorption capacity of 3.63 mmol/g at a low temperature of 303 K. Moreover, it showed appropriate selectivity factors of 6.28, 16.39 and 42.14 respectively for CO/CO<sub>2</sub>, CO/CH<sub>4</sub> and CO/N<sub>2</sub> gas pairs at the low pressure of 100 kPa. Significant stability of the sorbent in operation with its predominant monolayer adsorption was the other remarkable result of the investigation.

Another research team [12] investigated the CuCl/AC sorbent for CO separation from a syngas mixture in a VPSA process at ambient temperature (303 K) and 0.79 MPa. They also simulated the process to find an optimum result through the dynamic optimization with the Aspen Adsorption software. An adsorption result similar to that obtained by Gao et al. [11] revealed that the CuCl/AC adsorbent with the copper loading of 7 mmol/g AC has the high capacity of the reversible CO sorption and selectivity. The optimization result showed that the VPSA process could result in the CO purity of 98.1 vol % in a low concentration of the CO feed (32.3 vol %).

In this work, for the first time, a computational fluid dynamics (CFD) simulation approach was carried out to

simulate CO separation from a syngas mixture including CO, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub> through a CuCl/AC sorbent-based PSA process at 303.15 K and 1000 kPa. In this case, a 3D simulation of separation vessels with different dimensions and more realistic process conditions was considered using the COMSOL Multiphysics software to find optimum vessel dimensions and process conditions.

# 2. Theoretical

# 2.1. Adsorption isotherm

Adsorption isotherms are commonly used to develop an adsorption process, indicating how much of the adsorbate is adsorbed by the adsorbent at a constant temperature. Since there are different isotherms based on various assumptions and cases, the adsorption data are extended to models with realistic assumptions. Therefore, for CO sorption, a statistical study of the isotherm models is performed to identify the models that are the best possible and further to describe the analyzed adsorption processes [13].

Langmuir isotherm model was initially developed to describe gas adsorption on solid adsorbents such as activated carbon. Linear and nonlinear mathematical equations of the Langmuir isotherm model are as follows [14].

$$q_{e} = q_{m} \frac{K_{L}.C_{e}}{1 + K_{L}.C_{e}}$$
Nonlinear Langmuir isotherm model (1)  
$$\frac{1}{q_{e}} = \frac{1}{q_{m}} + \frac{1}{q_{m}.K_{L}.C_{e}}$$
Linear Langmuir isotherm model (2)

In these equations,  $q_e$  is the adsorption value in equilibrium (mol/kg),  $q_m$  is the maximum adsorption value (mol/kg),  $K_L$  is Langmuir adsorption constant (m<sup>3</sup>/mol), and C<sub>e</sub> is the concentration in equilibrium (mol/m<sup>3</sup>) [14].

The Freundlich isotherm model describes the

reversible and non-ideal adsorption process. Unlike the Langmuir isotherm model, this model is not limited to a single layer, and can be used for multilayer adsorption. This model has its nonlinear form Equation (3) and linear form Equation (4); and its parameters can be found when  $Log(q_e)$  is plotted based on  $Log(C_e)$ , which is a straight line with a slope

of 1/n and intercept of  $Log(K_F)$ .

$$q_{e} = K_{F}(\frac{C_{e}}{C_{0}})^{\frac{1}{n}}$$
Nonlinear Freundlich isotherm model
(3)
$$log(q_{e}) = log(K_{F}) + \frac{1}{n}log(\frac{C_{e}}{C_{0}})$$
Linear Freundlich isotherm model
(4)

In these equations, qe is the amount of adsorbed species in equilibrium (mol/kg), KF (mol/kg) is the Freundlich adsorption equilibrium constant, Ce is the concentration value at equilibrium ( $mol/m^3$ ), and C<sub>0</sub> is also the initial concentration of the gas  $(mol/m^3)$ . The type of convergence is indicated by the value of "n", where both parameters K<sub>F</sub> and n are temperature dependent. The value of 1/n is the absorption intensity or the level of inhomogeneity, which indicates the relative energy distribution and inhomogeneity of the sites associated with the adsorbent [14]. It should be noted that for equations 1 to 4, partial pressures are first converted into concentrations so that the original form of the equations does not change.

### 2.2. Process simulation

According to the results of previous studies, CuCl(7.0)/AC is one of the best adsorbents for

# conditions of the CuCl(7.0)/AC catalytic adsorption bed in a PSA process and the relevant physical characteristics (such as the length of the adsorption bed, the radius of the bed, the porosity of the adsorbent, the approximate size of the adsorbent particles, its mass density, etc.). Next, the feed gas conditions (such as the concentration of the components, density, flow rate, temperature, and pressure of the inlet gas, etc.) should be determined. In this regard, some essential parameters are extracted from literatures or calculated by a process simulation software, ASPEN HYSYS, to complete the simulation dataset. The physical characteristics of the adsorption bed are listed in Table 1. The feed properties (syngas) are also summarized in Table 2.

CO separation and purification from syngas

[11]. It is necessary to first determine the

# Table 1

Physical characteristics of the CuCl(7.0)/AC catalytic adsorption bed [12].

5	J 1	L 1	
Parameter/Variable	Symbol	Units	Value
Solid bulk density related to adsorbent	$\rho_{b}$	kg/m <sup>3</sup>	473
Adsorbent shape coefficient	ψ	-	0.86
Specific surface of adsorbent environment	$a_p$	m²/g	477
Pore diameter	$d_p$	m	$3.77\times10^{-9}$
Internal porosity of the bed	ε <sub>b</sub>	-	0.24
Internal porosity of the particle	ε <sub>p</sub>	-	0.21
Bed height	$H_{b}$	m	3

Bed permeability	K	$m^2$	$4.69\times10^{-9}$
Internal radius of the bed	R <sub>b</sub>	m	0.5
Radius of adsorbent particles	$\mathbf{R}_{\mathrm{p}}$	m	0.001

# Table 2

Feed properties (syngas).

Parameters/Variable	Symbol	Units	Value
Density	$ ho_g$	kg/m <sup>3</sup>	11.11
Dynamic viscosity	$\mu_{g}$	kg/m.s	$1.855\times10^{\text{-5}}$
Average molecular mass	Mw	kg/mol	0.0279
Pressure	$P_{g}$	kPa	1000
Temperature	$T_{g}$	K	303.15
Volumetric flow rate	$V_{g}$	m³/h	185
Gas compressibility coefficient	Z	-	0.9965
General gas constant	R	kPa.m <sup>3</sup> /mol.K	8.314

**Note:** Some parameters, such as the temperature  $(T_g)$ , pressure  $(P_g)$  and volumetric flow rate  $(V_g)$ , have been received from syngas feed conditions (Karun Petrochemical Company, F3XR+C6V, Bandar-e Mahshahr, Khuzestan Province, Iran). Some other required parameters such as the gas density  $(\rho_g)$ , gas viscosity  $(\mu_g)$ , enthalpy ( $\Delta$ H), thermal conductivity (K<sub>g</sub>), thermal capacity at the constant pressure (C<sub>p</sub>), thermal capacity at the constant volume (C<sub>v</sub>), and gas compressibility coefficient (Z) have been extracted from the ASPEN HYSYS software by considering a simple flow and selecting the Peng-Robinson equation of state.

# 2.3. Mathematical modeling

In this model, the heat transfer between the vessel and the environment is ignored, and the initial pressure of the vessel and the outlet gas pressure are considered constant.

In this process, an adsorption bed with a diameter of 1 m and a height of 3 m is assumed in the vessel, which is shown in Figure 1.



Figure 1. Representation of the adsorption bed and its dimensions along with meshing.

In the simulation of the adsorption process, one of the key parameters determining the adsorption rate of each syngas feed component in the CuCl(7.0)/AC adsorbent bed is its adsorption coefficient. The Langmuir and Freundlich adsorption coefficients of syngas components, including CO, CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub>, on the CuCl(7.0)/AC adsorbent can be directly calculated from the adsorption data in literatures (see the Appendix, Figure A1 and Table A1) [12], but these data for  $O_2$ adsorption on CuCl(7.0)/AC are not available. In the case of the adsorption of O<sub>2</sub> in CuCl(7.0)/AC, one can use the adsorption coefficients of this gas in adsorbents similar to CuCl(7.0)/AC. Then with a simple proportionality ratio, these coefficients can be converted to what is needed. O<sub>2</sub> is a linear molecule with a kinetic diameter (size) of 3.46 Å, which is close in size and shape to the  $N_2$ molecule (3.64 Å), so its adsorption properties

are used for the proportionality ratio (see the Appendix, Figure A2 and Table A2).

For gas separation, not only the adsorption capacity is essential, but also the adsorption selectivity is a key factor. In Figure A1, the adsorption equilibrium of CO, CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> gases is shown on the CuCl(7.0)/AC adsorbent at the operational temperature of 303.15 K. In Figure A1, it can be seen that the CuCl(7.0)/AC adsorbent has a good CO adsorption capacity and can selectively adsorb CO over other gases such as CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub>. The reaction between CuCl and CO is stronger with the formation of  $\pi$  complex bonds, and its reactions with CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> are of Van der Waals and electrostatic interactions, which are weaker [12].

All the reported and calculated data for the feed gas (CO, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub>) are summarized in Table 3.

Table 3

Summary	of the spec	cifications o	of the feed	d gas (CO	$CH_4$ , N <sub>2</sub>	$H_2$ and	O <sub>2</sub> ) used	d for the	simulation
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Parameters	СО	CH <sub>4</sub>	$N_2$	$\mathbf{H}_2$	<b>O</b> <sub>2</sub>	Units
ρ	11.15	6.5	11.15	0.8	12.8	kg/m <sup>3</sup>
μ	$1.857\times10^{\text{-5}}$	1.159 × 10 <sup>-5</sup>	$1.87 \times 10^{-5}$	$8.88\times10^{\text{-5}}$	$2.14\times10^{\text{-5}}$	kg/m.s
ν	$2.4882\times10^{1}$	$4.474\times10^{\text{-5}}$	$1.1525\times10^{\text{-}2}$	$1.0943 \times 10^{\text{-3}}$	$2.4984 \times 10^{\text{-}4}$	m/s
n	4.1841	-	-	-	-	-
С	$3.7847\times10^{1}$	$7.9627\times 10^{\text{-5}}$	$1.7518\times10^{\text{-}2}$	$1.6722\times 10^{\text{-3}}$	$3.9814\times10^{\text{-}4}$	mol/m <sup>3</sup>
$\mathbf{C}_0$	$3.3943 \times 10^{\text{-}2}$	$1.2254\times10^{\text{-5}}$	$1.5711\times 10^{\text{-3}}$	$2.0981\times10^{\text{-3}}$	$3.1104\times10^{\text{-5}}$	mol/kg
$C_p$	1.05875	2.3147	1.05949	14.143	0.92964	kJ/kg.K
$C_v$	0.7456	1.743	0.7477	9.988	0.6556	kJ/kg.K
Dĸ	$1.9023\times10^{\text{-8}}$	$2.5136\times 10^{\text{-8}}$	$1.9022\times 10^{\text{-8}}$	$7.0907\times10^{\text{-8}}$	$1.7798\times 10^{\text{-8}}$	m <sup>2</sup> /s
$K_{\rm F}$	4.0743	-	-	-	-	mol/kg
K <sub>L</sub>	-	20.71073	14.75931	15.20101	12.05879	m <sup>3</sup> /mol
m	95.43	0.01	4.42	0.03	0.11	-
М	70.0115	0.0128	3.22425	0.3058	0.0706	mol/h
Mw	29.0109	16.0429	28.013	2.016	32	kg/mol

p 950.6 0.2 44 4.2	1 kPa
q <sub>m</sub> - 0.41446 0.21373 0.083	17 0.25621 mol/kg
U 1961.0865 0.2055 90.831 0.616	55 2.2605 kg/h
v 175.8822 0.03163 8.14628 0.773	53 0.1766 m <sup>3</sup> /h
Y 0.9506 0.0002 0.044 0.004	42 0.001 mol

Darcy's law can be used to simulate the gas flow in the adsorption bed, of which the equation is expressed as follows:

$$\frac{\partial}{\partial t}(\varepsilon_{\rm b}.\rho_{\rm g}) + \nabla(\rho_{\rm g}.u) = Q_{\rm m}$$
<sup>(5)</sup>

In this equation, t is the time (s),  $\varepsilon_b$  is the porosity of the adsorption bed (dimensionless),  $\rho_g$  is the gas density (kg/m<sup>3</sup>), Q<sub>m</sub> is the mass flow rate of the gas (kg/m<sup>3</sup>.s), and u is the Darcy velocity or flow velocity (m/s) calculated by the Equation (6).

$$\mathbf{u} = -\frac{\mathbf{k}}{\mu_{g}} \nabla \mathbf{P} \tag{6}$$

In this equation, k is the permeability of the medium (adsorption bed) (m<sup>2</sup>),  $\mu$ g is the dynamic viscosity of the gas (kg/m.s), and P is gas pressure (Pa) [15, 16].

To determine the amount of gases adsorbed in the bed, the adsorption coefficients calculated and presented in the Appendix were used in the mass transfer equation, Equation (7), which gives the final concentration of each component i.

$$P_{l_i}\frac{\partial C_i}{\partial t} + P_{2i} + \nabla(-D_{e_i}\nabla C_i) + u\nabla C_i = R_i \quad (7)$$

where  $C_i$  is the concentration of each component i (mol/m<sup>3</sup>), t is the time (s), u is the gas velocity (m/s), and  $R_i$  is the reaction rate of component i, which is considered zero due to the absence of reactions.

 $\mathbf{D}_{e_i}$  is the effective diffusion coefficient and

is calculated as follows [17]:

$$D_{e_i} = \frac{\varepsilon_p}{\tau_i} D_{K_i}$$
(8)

where  $\varepsilon_p$  is the internal porosity of the adsorbents (dimensionless),  $D_{Ki}$  is the Knudsen diffusion coefficient (m<sup>2</sup>/s) and  $\tau_i$  the tortuosity coefficient (dimensionless), which is calculated based on the Millington and Quirk model as follows [18]:

$$\mathbf{r}_{i} = \varepsilon_{p}^{\frac{-1}{3}} \tag{9}$$

 $D_K$  (m<sup>2</sup>/s) is determined using Equation (10) [19]:

$$D_{K} = \frac{d_{p}}{3} \sqrt{\frac{8RT}{\pi M_{W}}}$$
(10)

where  $d_p$  is the diameter of the adsorbent pore (m), R is the universal gas constant (8.314 kPa.m<sup>3</sup>/mol.K), T is the gas temperature (K), and Mw is the molecular mass of the gas (kg/mol).

The parameters  $P_{1i}$  and  $P_{2i}$  in Equation (7) are also calculated as follows:

$$\mathbf{P}_{\mathrm{li}} = \boldsymbol{\varepsilon}_{\mathrm{p}} + \boldsymbol{\rho}_{\mathrm{b}} . \mathbf{b}_{\mathrm{i}} \tag{11}$$

$$\mathbf{P}_{2i} = (\mathbf{C}_{i} - \boldsymbol{\rho}_{p}, \mathbf{C}_{p_{i}}) \frac{\partial \boldsymbol{\varepsilon}_{p}}{\partial t}$$
(12)

where  $\rho_b$  is the adsorbent bulk density (kg/m<sup>3</sup>), and b<sub>i</sub> (that will also be represented by K<sub>L</sub>) is the Langmuir adsorption coefficient (m<sup>3</sup>/mol). (13)

 $\rho_p$  is the adsorbent density (kg/m<sup>3</sup>) which is calculated as follows:

 $C_{pi}$  is the concentration of component i (dimensionless), which is calculated as follows:

$$C_{p_i} = b_i \cdot C_i \tag{14}$$

Table	4
I GOIC	

 $\rho_p = \frac{\rho_b}{1 - \varepsilon_p}$ 

Initial and boundary conditions of the above equation
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Equation No.	Initial condition	Boundary conditions
		$r = R_{b} \Rightarrow -n.\rho_{g}.u = 0$
5	$\mathbf{t} = 0 \Rightarrow \mathbf{P}_0 = 101.325 \mathrm{kPa}$	$L = 0 \Rightarrow P = P_g$
		$L = H_b \Rightarrow P = 101.325 \text{ kPa}$
		$r = R_b \Rightarrow -n.N_i = 0$
7	$\begin{array}{c} t = 0 \\ L \neq 0 \end{array} \Rightarrow C_{0_i} = 0 \end{array}$	$L = 0 \Rightarrow C_i = C_{0_i}$
		$L = H_b \Rightarrow -n.D_{ei}\nabla C_i = 0$

After collecting the required data and performing preliminary calculations related to the gas feed parameters, the COMSOL Multiphysics 5.3 software was used to solve the equations using a computer with RAM: 16 GB, processor: Intel(R) Core(TM) i3-4160 and display adapter: GTX 1060 6GB. COMSOL uses the finite element method (FEM) to numerically approximate the solution of partial differential equations (PDEs). It has often been used by researchers to solve CFD problems [20-22]. Also, unsteady conditions are used here to calculate the bed length (using the residence time for the effective adsorption).

Since the experimental data of the gas adsorption isotherms in the CuCl(7.0)/AC adsorbent are presented in the batch mode of operation, therefore, for the continuous adsorption in an adsorption bed, a cylindrical vessel with the optional dimensions of 1 m in diameter and 3 m in height (which has been usually used in similar PSA processes with catalytic adsorbents) was considered. Also, a time interval of 1000 seconds with 200 steps (of 5 seconds) was considered for this operation. Several meshes were tested, and finally, with 5436 non-structural elements, no change was seen in the results, which is a sign of mesh independence.

#### 3. Results and discussion

# **3.1.** Mesh independence in the process simulation

In the investigation of mesh independence, the number of different mesh sizes with nonstructural finite elements in the absorption bed is used to eliminate the effect of the mesh on the simulation results. In this regard, the CO concentration profile in the bed in 300 s is considered as the basis of evaluation. In Figure 2, the concentration of the CO gas in some points of the bed with a number of different elements shows the complete independence of the mesh in the present work.



**Figure 2.** Mesh independency (the concentration of the CO gas in some parts of the adsorption bed vs. the number of meshes in 300 s).

# **3.2.** Concentration of gases in the adsorption bed

As mentioned before, the concentration of CO, CH4, N2, H2 and O2 in the adsorption bed is calculated and presented at 5-second intervals. As it can be seen in Figure 3, the concentration of CO, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub> in the adsorption bed at 303.15 K, the feed pressure of 1000 kPa and the output pressure of 101.325 kPa have been obtained at different times. At the very beginning of the adsorption process (i.e. after 5 s), the easy passage of H<sub>2</sub> through the adsorption bed is evident. In 25 s, it has completely traveled the length of the adsorption bed and has left the bed by getting separated from other components of the gas mixture. From here on, until the end of the adsorption process, the concentration of H<sub>2</sub> throughout the adsorption bed is in the range of 1.66  $\times$  10<sup>-3</sup> to 1.70  $\times$  10<sup>-3</sup> mol/m<sup>3</sup>, which remains close to the concentration of H<sub>2</sub> in the feed ( $1.67 \times 10^{-3} \text{ mol/m}^3$ ). After H<sub>2</sub>, N<sub>2</sub>, which is physically similar to CO (i.e., CO and N<sub>2</sub> have molecular masses of 28.0109 and 28.0130 kg/mol, and their molecular sizes are 3.67 and 3.64 Å respectively) passes through the bed in 25 s and leaves the bed entirely in 50 s. The concentration of N<sub>2</sub> remains constant throughout the adsorption bed and in the range of 0.02 mol/m<sup>3</sup>, which is close to its concentration in the feed  $(1.75 \times 10^{-2} \text{ mol/m}^3)$ . However, the selective separation of CO from N<sub>2</sub> can be optimally performed through the Cucontaining AC adsorbent, which can form a  $\pi$ -complex between CO and Cu ions [8, 10].

In 25 s,  $O_2$  also starts to pass through the adsorption bed and in 75 s this phenomenon is complete. From here on, the concentration of this gas throughout the adsorption bed remains constant and in the range of  $3.94 \times 10^{-4}$  to  $4.06 \times 10^{-4}$  mol/m<sup>3</sup>, which is close to the concentration of this gas in the feed  $(3.98 \times 10^{-4} \text{ m}^3)$ . CH4 also begins to pass through the adsorption bed in 25 s but is slower than H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> because it completely passes through the adsorption bed at 300 s. The

concentration of CH<sub>4</sub> now remains constant and in the approximate range of  $7.88 \times 10^{-5}$  to  $8.14 \times 10^{-5}$  mol/m<sup>3</sup>, which is almost equal to the concentration of this gas in the feed  $(7.96 \times 10^{-5} \text{ mol/m}^3)$ . Therefore, in about 300 s, all gases except CO pass through the bed and CO is well separated from the syngas mixture, so, the bed is ready for the discharge step.





Figure 3. Concentrations of CO, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub> in the adsorption process.

Figure 3 shows the concentrations of the gas at 1000 s; as time passes and the flow continues, CO also passes through the bed. It can be concluded that if the adsorption step in the bed exceeds 300 s, the concentration of the adsorbed CO decreases. On the other hand, if the adsorption step takes less than 300 s, part of the CH<sub>4</sub> remains in the bed, which reduces the concentration of CO and operation efficiency. It should be noted that between 300 to 1000 s, the concentration of CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub> remains almost constant, and only the concentration of CO changes in the bed.

The concentration of each gas component along the adsorption bed at different times is shown in Figure 4 to Figure 8. These figures show the adsorption of CO from the feed gas and the passage of other components (CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub>). A careful examination of the curves. especially the curves of the concentration of CO along the adsorption bed at different times (Figure 4), shows that the saturation region of the bed increases by the passing of time. It is a common phenomenon in column adsorption. Moreover, near 1 and 2 m of the bed length are exhausted after the

passing of 250 and 750 s respectively. It is also clear from the results that the saturation rate of the adsorption bed decreases by time. Reducing the length of the adsorption bed reduces the initial investment cost, simplifies the operation process and increases the economic efficiency of the process. However, it should be noted that this also increases the sensitivity of the system to schedule. Hence, small changes in the timing of the PSA process steps can significantly change the efficiency of the process. Investigating the effects of the cycle period for a given feed has shown that shorter cycles with the higher power and flow rates can improve separation. However, for the gas mixtures including CO, CO<sub>2</sub>, and N<sub>2</sub>, the separation performance strongly depends on the regeneration of the adsorbent. A shorter cycle is unsuitable in this case because it can reduce the regeneration performance of the adsorbent, which is controlled by the discharge capacity of the vacuum pump [23].



Figure 4. Changes in the concentration of CO along the adsorption bed at different times.



Figure 5. Changes in the concentration of CH<sub>4</sub> along the adsorption bed at different times.



Figure 6. Changes in the concentration of N<sub>2</sub> along the adsorption bed at different times.



Figure 7. Changes in the concentration of H<sub>2</sub> along the adsorption bed at different times.



Figure 8. Changes in the concentration of O<sub>2</sub> along the adsorption bed at different times.

# **3.3.** Effect of the feed flow rate

To investigate the effect of the feed flow rate on CO adsorption, changing the inlet feed pressure has been used. This is according to Darcy's law (velocity-pressure equation) in the simulation of the gas flow in the adsorption bed. As mentioned in section 0, Darcy's law (Equation (5)) uses the inlet gas pressure to the adsorption bed, permeability coefficient and dynamic viscosity of the inlet gas to calculate the axial pressure in the adsorption bed. Therefore, the only way to change the flow rate of the inlet gas is to change the inlet pressure at a constant outlet pressure (to increase the pressure difference along the bed). Thus, the concentration of CO in the adsorption bed at 300 s (the end of the adsorption step for the base feed pressure of 1000 kPa in this simulation), and for several other pressures, i.e. 700, 1300, 1600 and 2000 kPa is also investigated, and the results are shown in Figure 9.



**Figure 9.** Comparison of the concentration of the CO gas in the adsorption bed at 300 s and different inlet pressures (or different inlet flow rates).

As shown in Figure 9, as the inlet feed pressure increases, the CO concentration difference along the adsorption bed decreases, which means a reduction in CO adsorption and, thus, a decrease in the efficiency of the process. Although increasing the inlet feed pressure can reduce the duration of the absorption process, the efficiency of the process (final CO purity) is much more important. As a result, the pressure of 700 kPa is more suitable for the inlet feed pressure in the adsorption bed. As it can be seen in Figure 9, at 700 kPa and 300 s with a shorter bed

height of 0.5, CO is obtained with a purity of more than 99.8 %. On the other hand, increasing or decreasing the inlet feed pressure can significantly increase the initial costs and operating costs of the process. Therefore, using a feed pressure of less than 1000 kPa, equivalent to a 1 m long adsorption bed, to achieve CO with a purity of more than 99.5 %, requires further economic considerations.

# 4. Conclusions

In this work, the CFD modeling of CO purification from a syngas mixture in an

adsorption bed (3 m in length and 1 m in diameter) filled with cuprous chloride on the activated carbon support (CuCl/AC) was performed. The flow of CO, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub> in the bed was well simulated and it was shown that in about 300 s, all gases except CO passed through this bed and CO was well separated from the gas mixture. In 1000 s, CO also passed through the bed, of which it can be concluded that if the pressurizing (adsorption) time exceeds 300 s, the concentration of the separated CO will decrease. Also, if the pressurizing time is less than 300 s, part of the CH4 remains in the bed and reduces the concentration f the adsorbed CO, and hence the purification efficiency decreases significantly. By reducing the length of the absorption bed from 3 to 2 m, the efficiency of the absorption process will not change. The adsorption bed creates a large pressure drop (885 kPa), but finally, the output pressure from the adsorption bed (104.5 kPa) is suitable for the next process, which here is the phosgene production process. By increasing the pressure

(or flow rate) of the inlet syngas mixture, the duration of the process decreases, but on the other hand, the efficiency of the process decreases.

### Appendix

To calculate the adsorption coefficients of CO, CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> on the CuCl(7.0)/AC adsorbent, first, the data in Figure A1 was extracted. Next, the extracted data (in terms of partial pressures (kPa) were converted to adsorption isotherms in terms of the concentration of component (mol/m3) using Equation (15).

$$C_g = \frac{P_g}{Z.R.T_g}$$
(15)

where  $C_g$  is the gas concentration (mol/m<sup>3</sup>),  $P_g$  is the gas pressure (kPa),  $V_g$  is the gas volume (m<sup>3</sup>), Z is the gas compressibility factor (dimensionless), R is the universal gas constant (= 8.314 kPa.m<sup>3</sup>/mol.K), and  $T_g$  is the gas temperature (K).



**Figure A1.** Equilibrium CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> adsorption at different pressures on the CuCl(7.0)/AC adsorbent at 303.15 K [12].

In addition, according to Figure A1, it is clear that fitting a linear equation to CO adsorption, the equilibrium isotherm data will have a significant deviation. As a result, it is necessary to use the nonlinear least square (NLLS) method to determine the adsorption coefficients. Therefore, it is necessary to use the Freundlich equation (Equation (3)) for CO and then use the logarithm of the new numbers to find the linear fit. On the other hand, the Langmuir equation (Equation (2)) was used for CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> and then the new numbers were inverted to find the linear fit. The calculated adsorption coefficients for CO, CH<sub>4</sub>, N<sub>2</sub> and H<sub>2</sub> are presented in Table A1.

# Table A1

Calculated Freundlich and Langmuir constants for CO,  $CH_4$ ,  $N_2$  and  $H_2$ .

Con	Fr	eundlich consta	nts	Langn	nuir constants	
Gas	n	K <sub>F</sub> (mol/kg)	<b>R</b> <sup>2</sup>	q <sub>m</sub> (mol/kg)	K <sub>L</sub> (m <sup>3</sup> /mol)	R <sup>2</sup>
СО	4.18410	4.07430	0.9794	-	-	-
CH <sub>4</sub>	-	-	-	0.41446	20.71073	0.9944
$N_2$	-	-	-	0.21373	14.75931	0.9892
$H_2$	-	-	-	0.08317	15.20101	0.9937

As mentioned above, the adsorption coefficients for  $N_2$  on CuCl(7.0)/AC can be used to calculate the O<sub>2</sub> adsorption coefficient on CuCl(7.0)/AC. For this purpose and to

calculate the relevant proportionality ratio, the adsorption isotherms of  $O_2$  and  $N_2$  on the activated carbon adsorbent from reference [24] were used (Figure A2).



Figure A2. Equilibrium  $O_2$  and  $N_2$  adsorption at different pressures on the activated carbon adsorbent at 303.15 K [24].

Now, having the adsorption coefficient of  $N_2$  in the CuCl(7.0)/AC absorbent and the

adsorption coefficients of  $N_2$  and  $O_2$  in activated carbon, the adsorption coefficient of

 $O_2$  in the CuCl(7.0)/AC absorbent is easily calculated using proportional fitting. All these

coefficients are reported in Table A2.

# Table A2

Adsorption coefficients of O<sub>2</sub> and N<sub>2</sub> on activated carbon and CuCl(7.0)/AC adsorbents at 303.15 K.

Adaphant	Cas	Langmuir coefficients			
Ausorbent	$q_{\rm m}  ({\rm mol/kg})$		K <sub>L</sub> (m <sup>3</sup> /mol)	R <sup>2</sup>	
Activated carbon	$O_2$	3.95101	1.68173	0.9681	
Activated carbon	$N_2$	3.29598	2.05834	0.9626	
CuCl(7.0)/AC	$O_2$	025621	12.05879	0.9681	
	$N_2$	0.23373	14.75931	0.9892	

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