



## Sorption enhanced process by integrated heat-exchanger reactor assisted by fluidization concept for methanol synthesis



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### ABSTRACT

Coupling reactor has been identified as one of the most promising configurations for simultaneous production of methanol and hydrogen; as well stabilizing the atmospheric greenhouse gases level. In this work, methanol synthesis is carried out in exothermic side, which is a fluidized-bed reactor with in-situ water adsorption and supplies the necessary heat for the dehydrogenation of cyclohexane in endothermic side. Simulation results show that selective water adsorption from methanol synthesis in Fluidized bed Sorption Enhanced Thermally Coupled Reactor (FSE-TCR) leads to a considerable intensification of methanol production compared to zero solid mass ratio condition. Subsequently, a multi-objective optimization of FSE-TCR is conducted using the NSGA-II algorithm, and Pareto optimal frontiers are obtained in two cases including the maximum methanol production rate and selectivity. The Shannon's Entropy, LINMAP, and TOPSIS methods as three decision making approaches are used to select the final solution of Pareto front. The optimization results enhance about 214.3 and 280.5 ton day<sup>-1</sup> methanol production rate and CO<sub>2</sub> removal rate, respectively, based TOPSIS methods in comparison with the conventional methanol configuration. Furthermore, the optimization results represent 6.88 ton day<sup>-1</sup> enhancement in hydrogen production rate in comparison with the non-optimized configuration using the same catalyst loading and duty.

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### 1. Introduction

Energy is an essential factor in our lives. Nowadays, most of the energy is obtained from fossil fuel and it is non-renewable. Methanol is introduced as a fuel owing to its chemical and physical properties and it has proved to be an interesting automotive fuel. In the world today, methanol is one of the indispensable building blocks of the chemical industry.

In several processes such as methanol synthesis, an applicable solution to by-pass the thermodynamic limitations is the sorption-enhanced reaction process in a fluidized bed reactor. In this configuration, the equilibrium shifts toward the formation of more products via adsorbent solid particles, which are selective adsorbents adding to the reaction zone.

*Abbreviations:* FSE-TCR, fluidized bed sorption enhanced-thermally coupled reactor; FTCR, fluidized bed thermally coupled reactor; CMR, conventional methanol reactor; NSGA, non-dominated sorting genetic algorithm.

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In a fluidized bed reactor, the main advantages are low pressure drop, conversion improvement, excellent heat transfer capability, and elimination of diffusion limitations [1]. In order to solve some practical disadvantages of industrial packed-bed reactors, Wagiulla and Elnashaie [2] proposed a fluidized-bed configuration for methanol synthesis. In spite of the fact that the fluidized-bed reactor has several advantages, there are a few possible drawbacks such as: erosion of reactor internals and catalyst attrition and difficulties in reactor construction [3].

In this study, a novel idea of sorption-enhanced thermally coupled reaction process using zeolite 4A as a selective water adsorbent is proposed for methanol synthesis in the fluidized bed reactor.

The thermally coupling of endothermic-exothermic reactions can be carried out in various configurations such as direct, regenerative, and recuperative coupling reactor. A schematic flow pattern of these reactor configurations has been presented by Ramaswamy et al. [4,5]. Then, an experimental study of endothermic-exothermic reaction was done by Hunter and McGuire [6] by means of indirect heat transfer. Recently, Bayat and colleagues have considered several integrated configurations

**Nomenclature**

$a_b$	Specific surface area of bubble ( $\text{m}^2 \text{m}^{-3}$ )
$A_c$	Cross section area of each tube ( $\text{m}^2$ )
$A_r$	Archimedes number
$a'_s$	Specific surface area of adsorbent solid ( $\text{m}^2 \text{m}^{-3}$ )
$Cp_g$	Specific heat of the gas at constant pressure ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$Cp'_s$	Specific heat of the adsorbent solid at constant pressure ( $\text{J kg}^{-1} \text{K}^{-1}$ )
$C_t$	Total concentration ( $\text{mol m}^{-3}$ )
$D$	Reactor diameter (m)
$d_b$	Bubble diameter (m)
$D_i$	Tube inside diameter (m)
$D_o$	Tube outside diameter (m)
$d_c$	Catalyst diameter (m)
$d_s$	Adsorbent solid diameter (m)
$f_{\text{ads}}$	Volume fraction of adsorbent in emulsion phase
$F_i$	Molar flow of species I ( $\text{mol s}^{-1}$ )
$F_t$	Total molar flow per tube ( $\text{mol s}^{-1}$ )
$F^e$	Molar flow in emulsion side ( $\text{mol s}^{-1}$ )
$F^b$	Molar flow in bubble side ( $\text{mol s}^{-1}$ )
$\Delta H_{f_i}$	Enthalpy of formation of component i ( $\text{J mol}^{-1}$ )
$h'_f$	Gas-solid heat transfer coefficient ( $\text{W m}^{-2} \text{K}^{-1}$ )
$h_i$	Heat transfer coefficient between fluid phase and reactor wall ( $\text{W m}^{-2} \text{K}^{-1}$ )
$h_o$	Heat transfer coefficient between coolant stream and reactor wall ( $\text{W m}^{-2} \text{K}^{-1}$ )
$K$	Mass transfer coefficient for component i in fluidized-bed ( $\text{m s}^{-1}$ )
$K_w$	Conductivity of fluid phase S ( $\text{W m K}^{-1}$ )
$k'_g$	Gas-solid mass transfer coefficient ( $\text{m s}^{-1}$ )
$L$	Length of reactor (m)
$N$	Number of components used in the model ( $N=7$ )
$P_t$	Total pressure (bar)
$q$	Concentration of water adsorbed in flowing solids ( $\text{mol kg}^{-1}$ )
$q_e$	Equilibrium concentration of adsorbed water ( $\text{mol kg}^{-1}$ )
$R$	Universal gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$Re_t$	Reynolds number (-)
$r_i$	Reaction rate of component i ( $\text{mol kg}^{-1} \text{s}^{-1}$ )
$r_{bi}$	Reaction rate of component i in bubble phase ( $\text{mol kg}^{-1} \text{s}^{-1}$ )
$S'$	Mass flux of water adsorption ( $\text{kg m}^{-2} \text{s}$ )
$T_g$	Bulk gas phase temperature (K)
$T_s$	Temperature of catalyst phase (K)
$T'_s$	Temperature of flowing solids (K)
$T_{shell}$	Temperature of coolant stream (K)
$U$	Overall heat transfer coefficient between coolant and process streams ( $\text{W m}^{-2} \text{K}^{-1}$ )
$u_b$	Velocity of rise of bubbles ( $\text{m s}^{-1}$ )
$u_g$	Superficial gas velocity ( $\text{m s}^{-1}$ )
$u_{mf}$	Velocity at minimum fluidization ( $\text{m s}^{-1}$ )
$u'_s$	Real flowing solids velocity ( $\text{m s}^{-1}$ )
$y_i$	Mole fraction of component i in the fluid phase ( $\text{mol mol}^{-1}$ )
$y_{ib}$	Mole fraction of component i in the bubble phase
$y_{ie}$	Mole fraction of component i in the emulsion phase
$z$	Axial reactor coordinate (m)
Greek letter	
$\epsilon_{mf}$	Void fraction of catalytic bed at minimum fluidization
$\rho$	Density of fluid phase ( $\text{kg m}^{-3}$ )
$\rho_{\text{ads}}$	Density of adsorbent particle ( $\text{kg m}^{-3}$ )

$\rho_B$	Density of catalytic bed ( $\text{kg m}^{-3}$ )
$\rho_p$	Density of catalyst ( $\text{kg m}^{-3}$ )
$\eta$	Catalyst effectiveness factor
$\delta$	Bubble phase volume as a fraction of total bed volume
$\eta$	Effectiveness factor
$\mu$	Dynamic viscosity (Pa s)
$\rho_g$	Gas density ( $\text{kg m}^{-3}$ )
$\rho_p$	Particle density ( $\text{kg m}^{-3}$ )
$\rho'_s$	Flowing solid density ( $\text{kg m}^{-3}$ )
$\gamma$	Volume fraction of catalyst occupied by solid particle in bubble

of coupling reactor [7–10]. They also investigated the synthesis of methanol coupled with cyclohexane dehydrogenation reaction in the presence of zeolite 4A adsorbent particle solids in a packed bed reactor [11].

The composition of zeolite 4A solid particles is  $\text{Na}_{12}(\text{Si}_{12}\text{Al}_{12}\text{O}_{48})\cdot 27\text{H}_2\text{O}$ . Its high capacity of water adsorption makes it attractive in water separation and removal [12].

During methanol synthesis in the FSE-TCR, in-situ  $\text{H}_2\text{O}$  removal can lead to the displacement of water gas-shift equilibrium, and consequently, enhances the  $\text{CO}_2$  conversion into methanol using sorption-enhanced reaction process [13]. In sorption-enhanced reaction process, the discontinuity of the reactor operation is the main practical issue, because in the equilibrium state of the solid adsorbent, the separation effect is lost. Therefore, a periodic adsorbent regeneration is indispensable [13]. In order to solve this problem, a continuous regeneration of zeolite 4A is prepared in FSE-TCR based on desorption of water vapor. In general, dehydration of zeolites is carried out on a flow of carrier gas or under vacuum with an enhancement of temperature up to 300–400 °C, simultaneously [14]. The zeolite 4A crystal has rather good thermal stability. The reductions in water capacity accompanied by the change of its structure occur only above 1073 K [12].

The fixed bed configurations in the sorption-enhanced process have some noticeable drawbacks: Firstly, as the catalyst and adsorbent particles should be relatively large, ranging from millimeters to centimeters, their performance will be reduced owing to the diffusion limitations. Secondly, it is difficult to substitute the adsorbent particles inside the fixed bed reactor. Thirdly, the operation of regeneration reaction switch-type is not convenient. Fourthly, since the adsorbents and catalysts are fixed, hot spots may occur in the bed [15]. A fluidized bed configuration is probably a better choice in order to circumvent these drawbacks.

Johnsen et al. [16] have proven that gas-solid contact in a laboratory scale bubbling fluidized bed reactor is sufficient to achieve close approximation to equilibrium conditions. The idea of fine solid particles (flowing solids) and contacting gas inside a fluidized bed reactor was patented nearly fifty years ago [17]. They have patented a fluidized-bed process using calcium based sorbent and reforming catalyst.

The subject of methanol synthesis and its adsorption has been widely studied in various types of reactors by Westerterp and coworkers [18–22]. In 1987, Kuczynski et al. worked on methanol adsorption on amorphous LA-25 low-alumina cracking adsorbents in a counter-current gas-solid-solid trickle flow reactor to produce methanol. It was proved that removing product from the reactor lead to a higher conversion of the reactants [18]. Westerterp et al. compared the intensified process with the conventional methanol synthesis in a highly optimized Lurgi process [20]. The reduction in the recirculation rate and pressure drop inside the reactor caused a significant energy saving in the synthesis loop. Recently, Van Bennekom et al. have investigated methanol synthesis, thermodynamically, accompanied by in situ condensation of methanol

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