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Thermocatalytic hydrogen production from the methane in a fluidized bed with activated carbon catalyst

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Abstract

A fluidized bed reactor made of quartz with 0.055 m i.d. and 0.65 m in height was employed for the thermocatalytic decomposition of methane to produce CO_2 free hydrogen. The fluidized bed reactor was proposed in order to overcome the reactor plugging problem due to carbon deposition, which was resulted in the shut-down of the fixed bed reactor system. Several kinds of activated carbons were employed as the catalyst to examine the reaction activity. The experimental results in this study were compared with that of fixed bed reactor. The reaction rate and deactivation of carbon catalyst were similar to that of lab scale fixed bed reactor system. The deactivation due to carbon deposition was verified with the SEM images of fresh and used carbon catalysts. The effects of gas velocity, reaction temperature and particle size on the reaction rates were also investigated. From the experimental results of this study, the optimum operating conditions for fluidized bed were also determined.

Keywords: Hydrogen; Thermocatalytic decomposition; Activated carbon; Fluidized bed reactor; Methane

1. Introduction

Hydrogen has been thought of the energy source for the future, in terms of the most environmentally acceptable energy source. The problem is that there is no natural resource which produces hydrogen and therefore, it is not a primary fuel in the nature [1]. Steam reforming of natural gas is the most efficient and widely used process for the production of hydrogen. The energy requirement per mole of hydrogen produced for overall process is equal to 40.75 kJ/mol H_2. However, the total CO_2 emissions from steam reforming process reaches up to 0.43 moles CO_2 per each mole H_2 produced. To produce H_2 without CO_2 emissions, thermal decomposition of methane becomes influential and is studied [2].

Natural gas can be thermally decomposed into carbon and hydrogen. The carbon can be sequestered or sold as a materials commodity. Thus hydrogen can be produced by thermal decomposition from natural gas cleanly without the production of CO_2 [3].

The alternative method for hydrogen production with sequestration of carbon is the thermocatalytic decomposition of natural gas. Thermocatalytic decomposition of methane occurs at elevated temperature and results in the formation of hydrogen and elemental carbon:

$$CH_4 = C + 2H_2 \quad \Delta H^o = 75.6\,\text{kJ/mol}$$

Due to the absence of oxidants (e.g. H_2O and/or O_2), no carbon oxides formed in the reaction. Thus, the main advantages of this approach are in relation to the production of hydrogen in a single step, with no need for gas conditioning (e.g. CO_2 removal) stages required by conventional technologies (e.g. steam reforming, partial oxidation). The energy requirement per mole of hydrogen produced (37.8 kJ/mol H_2) is somewhat less than other conventional processes of hydrogen production, such as steam reforming process (63.3 kJ/mol H_2). Methane decomposition reaction is an endothermic process and temperature above 700 °C is required [4].

There have been attempts to use catalysts in order to reduce the maximum temperature of thermal decomposition of methane. Metal catalysts, including Ni, Fe, Co and others, have been most commonly used for methane decomposition. However, there was a catalyst deactivation problem

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associated with the carbon buildup on the catalyst surface [2,5]. In order to remove the produced carbon from the reactor and regenerate the original activity of the metal catalyst, the catalyst surface was burned-off. As a result, the amount of CO_2 produced is comparable with that of the conventional processes. Another serious problem arising from the oxidative regeneration of metal catalysts relates to unavoidable contamination of hydrogen with carbon oxides, which would require an additional purification step. Our technical approach is based on thermocatalytic decomposition of hydrocarbons over the carbon-based catalysts in air/water-free environment. The use of carbon catalysts offers the following advantages compared with other metal catalysts (e.g. Ni, Fe, Co and others): (a) no need for the regeneration of the catalysts by burning production carbon; (b) no contaminations in hydrogen with carbon oxides and consequently, no need for the additional gas purification; (c) production of a valuable byproduct—elemental carbon [1,3].

Recently, several researches for catalytic decomposition of methane over activated carbon catalysts were conducted in a small packed bed reactor system [1,6,7]. In a packed bed reactor system, activated carbon showed good catalytic activity at the beginning of the reaction and slowly deactivated. The problem of this system was the carbon deposition over activated carbon catalysts. As the reaction proceeds the produced carbon deposited on the surfaces of the activated carbons and the particle size of activated carbons got bigger and bigger. In the long run, the reactor was completely filled with produced carbons and the flow path for reactant gas was blocked. Therefore, for the continuous process of catalytic methane decomposition over activated carbon catalyst, the activated carbon catalysts must be removed from the reactor after certain residence time in order to maintain the reaction activity and to avoid plugging by produced carbons.

In order to overcome these problems, a fluidized bed reactor was proposed in this study. Fluidized bed reactors have been widely used in the chemical, metallurgical and petroleum industries. A fluidized bed system does provide constant flow of solids through the reaction zone, which makes it particularly suitable for the continuous addition and withdrawal of carbon particles from the reactor. In a fluidized bed reactor, the bed of carbon catalysts behaves like a well-mixed body of liquid, giving the rise to high particle-to-gas heat and mass transfer rates. In this study, the batch type fluidized bed reactor system was tested and the parameter effect on reaction rate was investigated. Furthermore, the experimental results of this study were compared with that of fixed bed reactor [6,7].

2. Experimental

Methane (99.95 vol.%) was used without further purification. Samples of carbon catalysts were obtained from domestic manufacturers in Korea. Basically two different types of activated carbons were employed. One is derived from coconut shell (designated here as CCN-SCR, CCN-UN and SCR; UN means the manufacturer name) and the other is from coal (designated as CL-SCR, CL-GU, and CL-CI). Physical and chemical properties of employed carbon catalysts were given in Table 1.

A schematic diagram of fluidized bed reactor used in our experiment is shown in Fig. 1. The fluidized bed reactor was made of quartz with i.d. of 0.055 m and 0.65 m in height. The amount of carbon catalysts was used about 20 g. The methane flow rate was controlled by mass flow controller. A feed stream of methane was preheated to 400 °C and entered the bottom of the reactor and contacted with the fluidized bed of carbon catalysts at 850 °C in the reaction zone, where thermocatalytic decomposition of methane occurred. Temperature was monitored by the thermocouple in the middle of the bed. In order to avoid the direct contact between the thermocouple and fluidized bed materials, the thermocouple was inserted in a quartz tube of 0.5 mm i.d. so that the effect of catalytic activity by the metal thermocouple in the bed was eliminated. In order to find out the effect of gas velocity which is the one of the major operation variables in the fluidized bed, the gas velocity was changed from minimum fluidization velocity (U_{mf}) to $4U_{mf}$ ranges and the $1U_{mf}$ is corresponding to space velocity of $0.9\,l/g_{cat}\,h$. In the fluidized bed operation, particle size is a very important factor and it is known that particle type of Geldart A is best for the smooth fluidization [8]. In order to maintain the good fluidization quality of activated carbon particles, the delivered activated carbons (about 1 mm) were crushed and sieved and the particle size of 50–300 μm were selected for the experimental test.

The exit gas from the top of the reactor was sampled with a gas tight syringe through a septum and the reaction products were analyzed by a gas chromatography (TCD detector, carrier gas of Ar). The characterization of carbon catalysts before and after reaction was analyzed by SEM.

Table 1
Physical properties of employed activated carbon catalysts

Carbon catalysts (origin)	CCN-SCR (coconut)	CCN-UN (coconut)	CL-SCR (coal)	CL-GU (coal)	CL-CI (coal)
ρ_s (g/cm^3)	1.5929	1.6793	1.8227	1.6124	1.8646
ρ_b (g/cm^3)	0.7412	0.4464	0.8142	0.6313	0.7013
U_{mf} (m/s)	0.21	0.50	0.22	0.24	0.88
U_t (m/s)	19.59	20.25	22.74	19.60	23.24
Surface area (m^2/g)	966	978	912	860	950

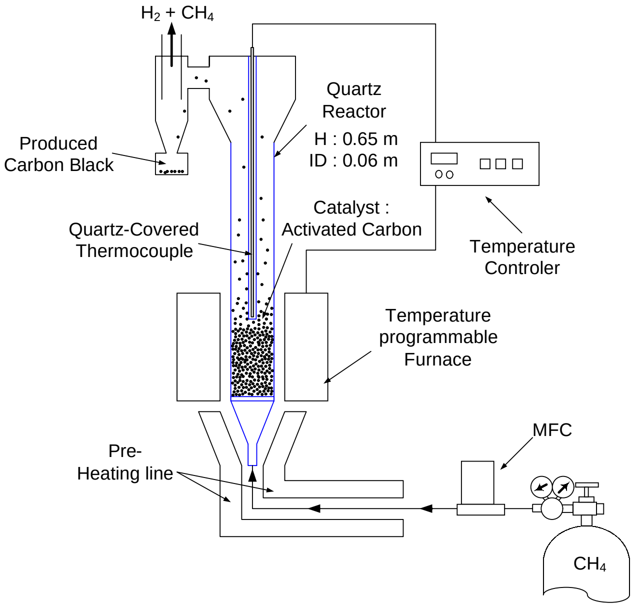

Fig. 1. A schematic diagram of experimental apparatus.

3. Results and discussion

3.1. Effect of types of activated carbon

The methane conversion as a function of time with different types of activated carbons at the temperature of 850 °C and gas velocity of $1U_{\mathrm{mf}}$ were shown in Fig. 2. As shown in Fig. 2, no significant difference was observed among different samples of activated carbons and the activated carbon catalysts showed high activity at the beginning of the reaction and were deactivated rapidly regardless of types of coal or coconut shell. After 4 h of reaction, most of activated carbons had 20–60 m^2/g of surface area. This indicated that the deactivation of activated carbon catalyst resulted from the blocking of pore mouth by the deposited carbon. The CCN-SCR sample showed better activity among the samples at the beginning of the reaction but after 4 h reaction, the activity of CCN-SCR was almost same as that of other activated carbons. Therefore, the slight difference of reaction rates among the employed catalysts depends on the structure of pore geometry and the deposition patterns of produced carbons. It was also found that the deactivation trend showed similar pattern with an earlier work in fixed bed reactor system [1,3] and it means that reaction mechanism was similar for both reactors. Fig. 3 showed SEM images of the surfaces of activated carbon before and after the reaction for activated carbon of CCN-SCR and CCN-UN. It showed that for the sample of CCN-SCR the carbon deposition on the catalyst surface was in the form of carbon filament which was also observed with metal catalyst [5]. However, for the sample of CCN-UN, the surface was covered with the produced carbons and no carbon filaments were observed. We did not carry out more intensive investigation on this phenomena and it was assumed that the trace of metal components such as Na, K, Fe in the activated carbon gave the site for carbon filament growth. Therefore, it can be said that the filamentous carbon formation depends on the trace metal in the ash of the activated carbon and the types of activated carbon and the operating condition of the reaction.

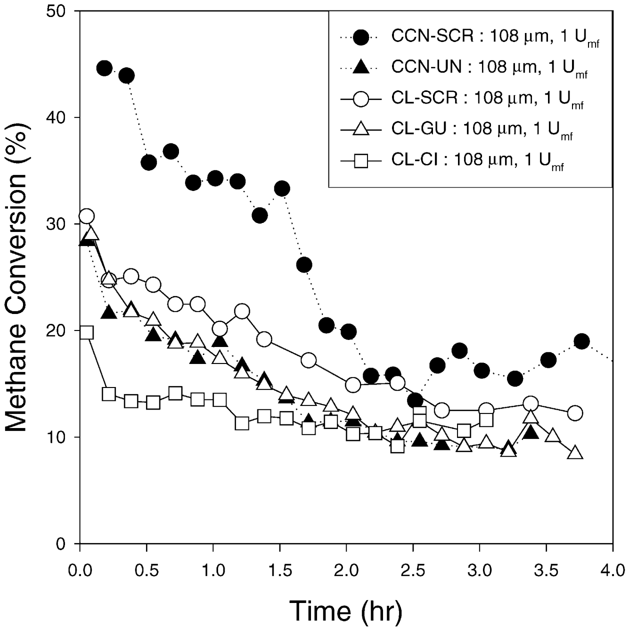

Fig. 2. The methane conversion as a function of time with different types of activated carbons at the temperature of 850 °C and gas velocity of $1U_{\mathrm{mf}}$.

3.2. Effect of reaction temperature

Fig. 4 showed the effect of reaction temperature on methane conversion over activated carbon of CCN-UN at the gas velocity of $1U_{\mathrm{mf}}$. As expected, the higher reaction temperature resulted in the higher initial reaction rates. However, the reaction rates decreased significantly with time at the higher reaction temperature. Because the higher reaction rates means the higher carbon production and the produced carbons deposited on the active sites of the activated carbon thus the deactivation of catalyst was accelerated. From the previous study of methane decomposition over activated carbon in fixed bed reactor, it was found that the reaction order was 0.5 [6] and the initial rates in the fluidized bed reactor were extrapolated. Fig. 5 showed the Arrhenius plot for methane decomposition over activated carbon of CCN-SCR. The activation energy was determined from the Arrhenius plot by assuming that fluidized bed was either plug flow or mixed flow. The experimentally determined activation energy was about 140 kJ/mol. The activation energy obtained by other work was reported to be 190–200 kJ/mol [1,6] and which is similar value as this study. Also, the experimentally obtained activation energy of 140 kJ/mol is much lower

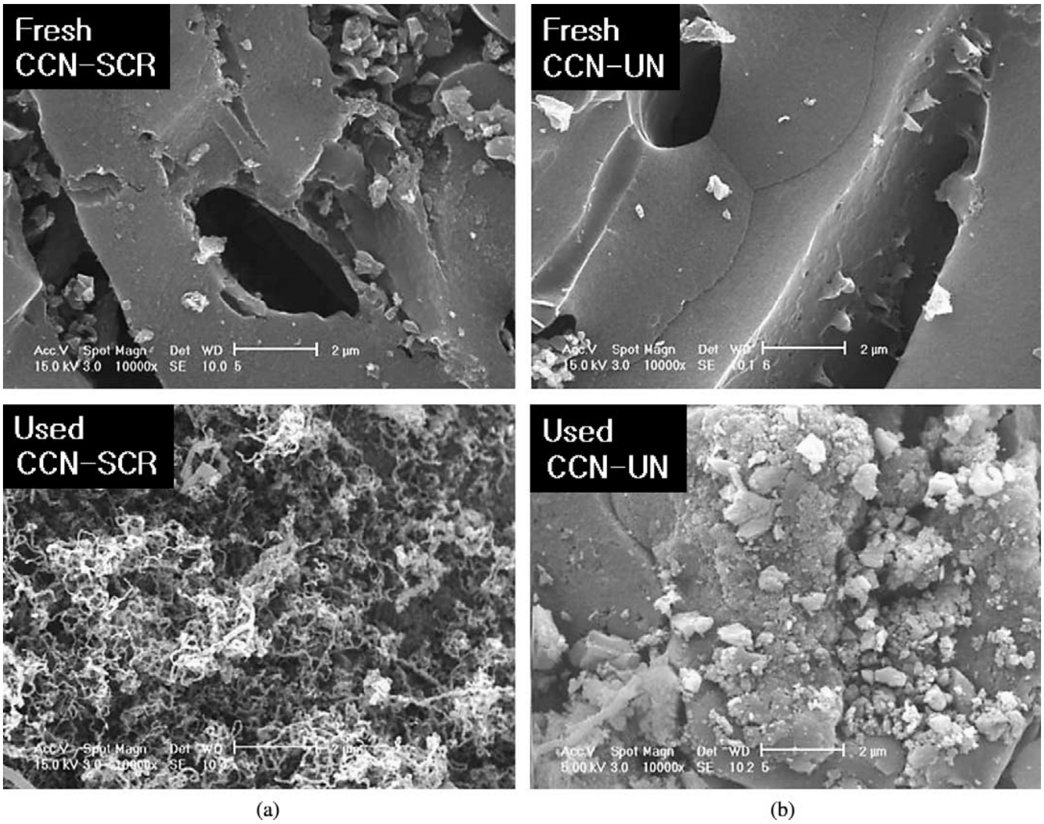

Fig. 3. SEM images of the surfaces of activated carbon before and after the reaction for activated carbon of CCN-SCR (a) and CCN-UN (b).

than the methane C–H bond energy of 440 kJ/mol. This suggested that the structure of active sites in these activated carbons and the reaction mechanism may be the same.

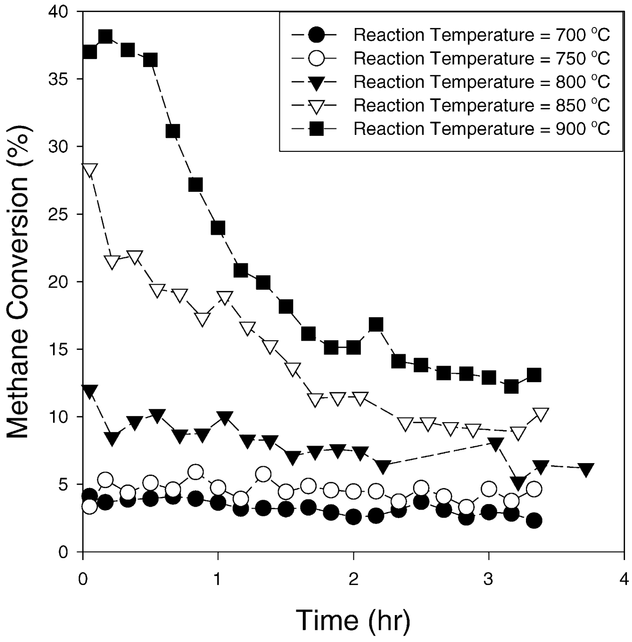

Fig. 4. The effect of reaction temperature on methane conversion over activated carbon of CCN-UN at the gas velocity of $1U_{\mathrm{mf}}$.

3.3. Effect of gas velocity

It is well-known that the gas velocity is the most important parameter in the fluidized bed reactor operation be-

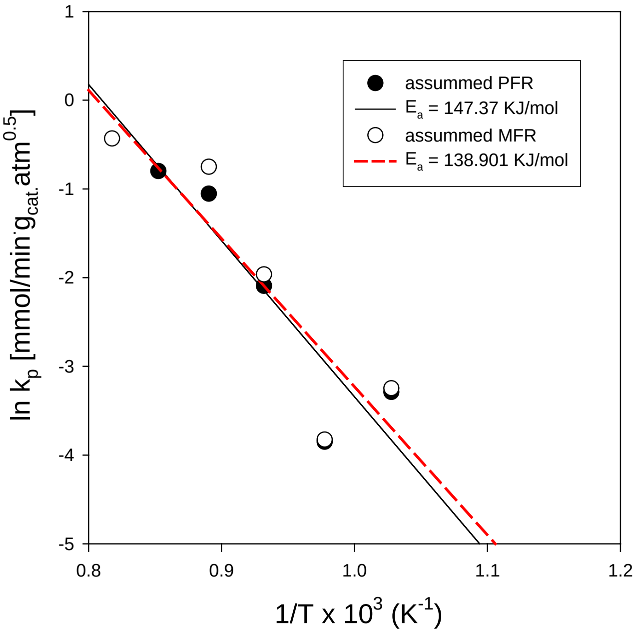

Fig. 5. Arrhenius plot for methane decomposition over activated carbon of CCN-SCR.

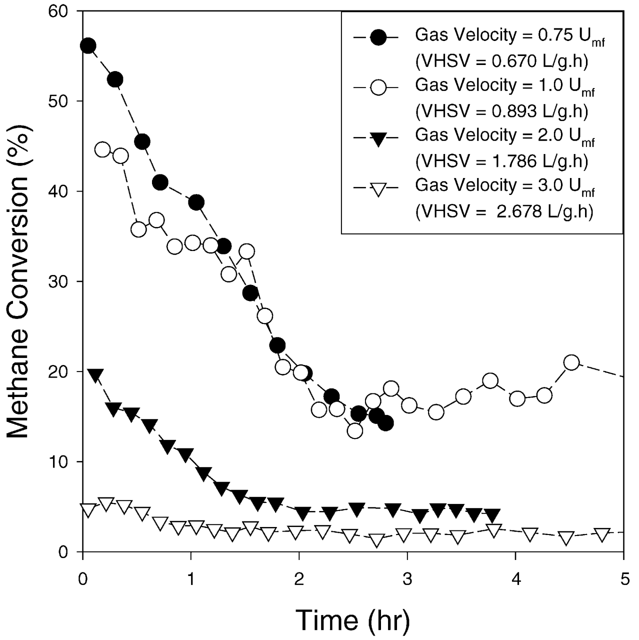

Fig. 6. The effect of gas velocity on the methane conversion over activated carbon of CCN-SCR at the temperature of 850 °C.

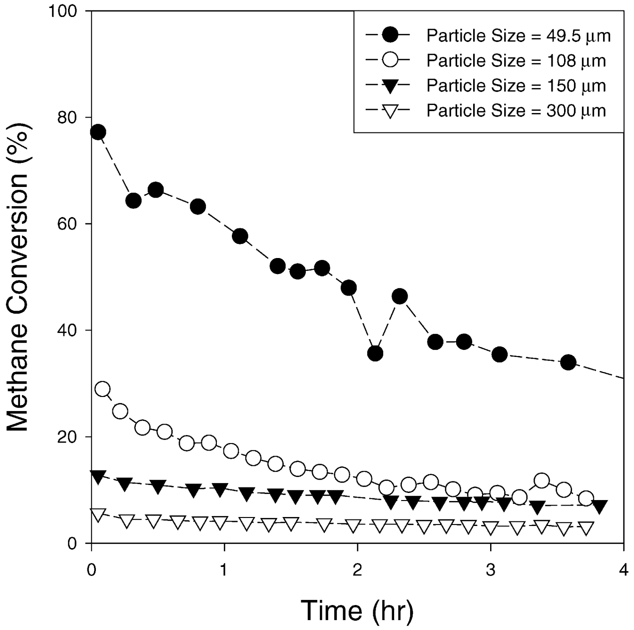

Fig. 7. The effect of particle size on the methane conversion over activated carbon of CL-GU at the temperature of 850 °C.

cause the fluidization quality or gas–solid contacting pattern is strongly dependent on gas velocity. Fig. 6 showed the effect of gas velocity on the methane conversion over activated carbon of CCN-SCR at the operating temperature of 850 °C. In fluidized bed, it is convenient to express the gas velocity in terms of minimum fluidization velocity so that the flow regime of fluidized bed is easily understood. The gas velocity of $1U_{\mathrm{mf}}$ is equivalent to space velocity of 0.9 $\mathrm{l/g_{cat}}$ h.

As can be seen in Fig. 6, the effect of gas velocity on the conversion was significant in the fluidized bed reactor. Unlike, the fixed bed operation, in the fluidized bed operation it is assumed that all the gas in excess of that required for minimum fluidization passed through the bed as bubbles. Therefore, the higher gas velocity increased the number of bubbles and the size of bubble and these bubbles may exit the reactor without effective contacting with activated carbon catalysts. Thus the increased gas velocity reduced the residence time in the reactor as well as lowering the contacting efficiency between gas and carbon catalyst due to bubble formation. The above mentioned hydrodynamic characteristics of fluidized bed explained why the gas velocity effect on the methane conversion was significant. However, the lowering the gas velocity in fluidized bed means the smaller throughput per unit volume of reactor, the optimum gas velocity should be chosen in terms of hydrogen production rates and methane conversion.

3.4. *Effect of particle size*

For the efficient fluidized bed reactor operation, it is also important to find out the proper particle size as well as proper gas velocity. The different sizes of activated carbons were prepared by pulverizing and sieving. Fig. 7 showed the particle size effect on the methane conversion over activated carbon of CL-GU at the operating temperature of 850 °C. As can be seen in Fig. 6, the smaller particles showed the higher reaction activity and it is believed that smaller particles have the higher surface area/particle volume and a mass transfer effect may exist. However, it was also observed that the effect of particle size on the methane conversion was insignificant after long period of time was reached. Another effect of particle size on conversion was the fluidization quality. In fluidization, it was known fact that Geldart A type particle in fluidization showed smooth fluidization and this means better contacting efficiency between gas and solid than other types of particle. Since the particle size of 108 μm belongs to Geldart A type particle [8], it is believed that the higher methane conversion was obtained [8]. Therefore, the higher surface area and smooth fluidization quality for the activated carbon of 108 μm particles resulted in the higher methane conversion in the fluidized bed reactor.

4. Conclusions

The characteristics of the thermocatalytic decomposition of methane in the fluidized bed reactor with activated carbons were investigated and experimental results were obtained.

The employed activated carbon catalysts showed good catalytic activity at the beginning of the reaction and deactivated rapidly due to carbon deposition on the active site of the catalysts regardless of types of activated carbons. The carbon deposition resulted in the deactivation of the catalyst and it was either in the form of carbon filaments or carbon agglomerates. The effect of reaction temperature and particle size of catalyst on the reaction rate was significant at the initial rate and after 3–4 h of reaction the effect of temperature and particle size became negligible. Experimentally determined reaction rates and activation energy of fluidized bed were similar to that of fixed bed experimental data and it means that reaction mechanism is almost similar in both reactors.

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