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Passive production of synthesis gas from liquid methanol using a packed bed of porous material particles

Kunito Okuyama *, Kanoko Ichimi, Masato Takazawa, Asami Natori, Mikako Tanaka

Department of Chemical Engineering Science, Yokohama National University, 79-5 Tokiwadai, Hodogaya, Yokohama 240-8501, Japan

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ABSTRACT

The passive production of synthesis gas from liquid methanol using a packed bed of porous material particles supporting a catalyst is investigated. Heating of the upper portion of a vertical tube packed with the porous particles where the bottom is immersed in liquid methanol is expected to cause steady upward fluid flow due to capillary action enhanced by evaporation. The emergence of a dry region and a resulting increase in temperature can produce synthesis gas due to catalytic reaction, which then flows out of the top end of the tube. In the proposed process, the capillary force, which is dependent on the local liquid content in the porous bed, is balanced locally with the gravitational force and the viscous forces acting on the liquid and vapor. The distributions of the liquid content, flow rates, pressures, and temperatures of liquid and vapor along the tube axis are calculated using a one-dimensional model based on the mass, force, and energy balances for each phase. The experimental results indicate the validity of the process, that is, the induction of steady fluid flow, the emergence of a dry region, temperature increase to the reaction level, and the products of the reacted gases. The behavior of liquid-vapor flow induced by phase-change in a packed bed and the factors that characterize the process and affect the performance are discussed.

1. Introduction

The reactions for the production of hydrogen from methanol (catalytic decomposition and/or steam reforming), which proceed at low temperatures of approximately 200–300 °C, are well known as associated with hydrogen supply to fuel cells, and have also received attention with respect to a reduction of exergy loss through combustion and the exergy enhancement of low-temperature thermal energy to that of hydrogen [1], chemical recuperation [2] in gas turbine systems [3,4], fuel cells [5], and internal combustion engines [6–8], and the storage/transport of renewable energy and/or process waste heat [9]. Conventional apparatus for these reactions is typically composed of a serial connection of a feed pump, preheater, evaporator, super-heater for methanol (and that for water in steam reforming), and a catalytic reactor. The process in each component is different in terms of the temperature level and dependence, fluid properties, and the heat transfer mode. Therefore, fluid flow and heating in these components must be controlled so that product gases with the desired rate and composition can be achieved without interactions between the components such as flow oscillation.

Here, we consider a simple reactor consisting of a packed bed in a tube filled with porous material particles that support a catalyst, as shown in Fig. 1. The lower end of the tube is immersed in liquid methanol while the upper side-wall is in contact with a heat source over an extensive area. Liquid methanol is absorbed into the packed bed due to the capillary action and then evaporates due to the heat from the heat source. If a dry region is formed in and around the heated region, and the temperature of the dry region increases up to the reaction level, then synthesis gas will be produced catalytically according to the decomposition reaction expressed in Eq. (1), and will then flow out of the upper end of the tube.

$$CH_3OH \rightarrow CO + 2H_2 \quad \Delta H_r{}^0 = 90.6\ \text{kJ/mol} \tag{1}$$

Liquid to compensate for the consumption due to evaporation and the reaction is continually drawn from the bottom due to capillary action and pre-heated before reaching the evaporation interface. Such a reactor involves the functions of liquid fuel supply, preheating of liquid/vapor, evaporation of liquid, and reaction, so that all processes can proceed simultaneously and passively by the heat supplied from a heat source. The packed bed allows for

* Corresponding author.
E-mail address: okuyama-kunito-tg@ynu.ac.jp (K. Okuyama).

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Nomenclature

A_c	cross section of the reactor tube (m^2)
a	pre-exponential factor in the Arrhenius equation (mol/(m^3 s Pa))
c_{pl}, c_{pv}	specific heat of liquid and vapor (J/(kg K))
E	activation energy (kJ/mol)
h_{fg}	latent heat for vaporization (J/kg)
K	permeability (m^2)
K_{rl}, K_{rv}	relative permeability of liquid and vapor (–)
k_{eff}	effective thermal conductivity (W/(m K))
l_p	perimeter of reactor tube (m)
M_{CH3OH}	molecular weight of methanol
$\dot{m}_v$	mass flow rate of vapor (kg/s)
p_c	capillary pressure (Pa)
p_{CH3OH}	partial pressure of methanol vapor (Pa)
p_l, p_v	pressure of liquid and vapor (Pa)
Q	heating rate in heating region (=$q'' l_p x_2$) (W)
Q_{ev}	heating rate for evaporation (W)
Q_h	heating power (W)
Q_r	heat absorption rate for reaction (W)
$Q_{s,l}$	heating rate as the sensible heat of the liquid (W)
$Q_{s,v}$	heating rate as the sensible heat of the vapor (W)
q''	wall heat flux (W/m^2)
R	universal gas constant (J/(mol K))
s	liquid saturation (–)
T_b	local temperature in packed bed (°C)
T_l, T_v	temperature of liquid and vapor (°C)
T_{lb}	bulk liquid temperature (°C)
T_{eq}	equilibrium temperature (°C)
T_{sat}	saturation temperature (°C)
u_v	space velocity of vapor in dried region (m/s)
x_1	position of lower end of dried region (m)
x_2	position of lower end of heating region (m)
x_3	position of maximum vapor pressure (m)
x_4	position of lower end of two-phase region (m)
x_L	location at the bottom of reactor tube (m)
y	yield of reaction (–)

Greek symbols

ΔH_r	reaction heat (kJ/mol)
η	heat utilization efficiency for methanol process (–)
η_d	heating efficiency in the dried region (–)
ν_l, ν_v	kinematic viscosity of liquid and vapor (m^2/s)
ρ_l, ρ_v	density of liquid and vapor (kg/m^3)
σ	interfacial tension (N/m)
ϕ	porosity (–)

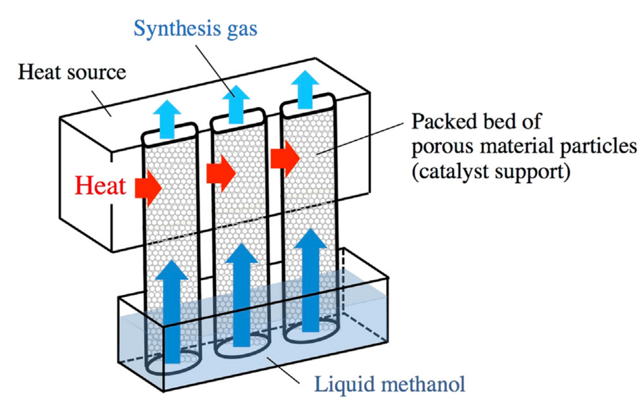

Fig. 1. Schematic diagram of the packed bed reactor to passively produce synthesis gas from liquid methanol.

the arbitrary shape of this reactor, so that its surface can be fixed to the piping of a hot fluid flow or a power dissipation device as the heat source without the rearrangement of pre-existing facilities. To make the continuous production of reacted gas possible, it is necessary that the dry region be formed above the evaporation region in the upper part of the packed bed, that liquid and vapor flow upward steadily due to capillary force, and that the temperature of the dried region reach the level of the reaction temperature (150–200 °C).

Fluid flow induced by heating in a packed bed and the resulting distributions of liquid content, local pressures of vapor and liquid, capillary pressure, and fluid temperatures are calculated for a methanol evaporation/decomposition system using a simple model based on the mass, force, and energy balances for liquid and vapor flows in the bed. Variations of these quantities for an increase of the heating rate were examined under conditions where the steady-state upward flow is ensured. An experiment was then conducted using a packed bed reactor, the size of which was set to be equivalent to that of the calculation. The emergence of the dry region, the temperature increase in the bed, the production rates of vapor and gases, composition of the reacted gases, yield of the reaction, and the efficiency of heat utilization were examined. The behavior of liquid-vapor flow induced by phase-change in the packed bed and the factors that characterize the process and affect the performance are discussed below.

2. Model of fluid flow and reaction in a heated packed bed

Fig. 2 shows a one-dimensional model of the reactor. The reactor is composed of a vertically placed single straight tube in which small porous particles that support the catalyst are tightly packed from the bottom to the top. The tube has a length of x_L (m) and a cross section of A_c (m^2). The top end of the tube is open while the bottom end of the tube is immersed in liquid methanol at room temperature, so that the liquid is absorbed into the bed due to capillary action. Absorption continues until the capillary forces that

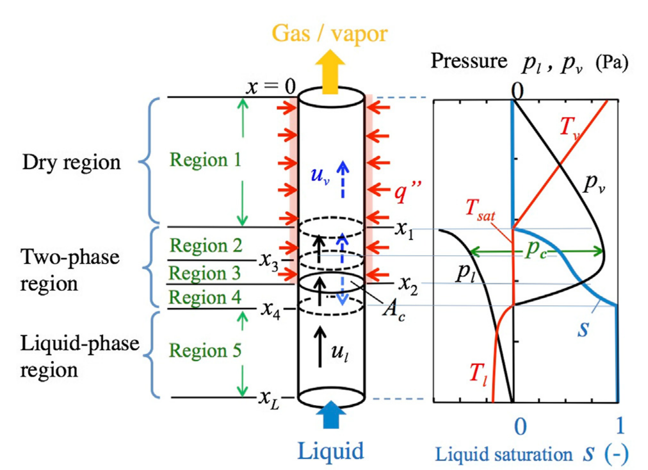

Fig. 2. Model for the packed bed reactor and change in liquid saturation due to heating.