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Hydrodynamics of multiphase flow in a trickle-bed filled with small particles under the supercritical condition

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HIGHLIGHTS

- The SCF was introduced into a TBR filled with small particles.
- The SCF possessed both non-liquid and liquid-like properties at the same time.
- A correlation used to predict the pressure drop with subcritical fluids was proposed.

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ABSTRACT

Hydrodynamics experiments with respect to supercritical and subcritical fluids were conducted in a laboratory-scale trickle bed reactor filled with relatively small particles of 0.67–1.32 mm in diameter. Residence time distribution was measured with tracer injection, and the results indicated that the supercritical fluids (SCF) have non-liquid-like features. From the pressure drop fluctuations, the pulsing flow was observed with the increase of the supercritical fluid mass flux; clearly, it shows that SCFs possess liquid-like property. Based on the empirical relationship proposed by Al-Naimi et al. (2011), the experimental data for subcritical fluids could be well correlated, which results in a new correlation in the predication of the pressure drop for fluids at subcritical conditions.

1. Introduction

Trickle-bed reactors (TBRs) are widely used gas–liquid–solid multiphase reactors in industrial practices, in which liquid and gas flow concurrently downward through a packed bed of catalyst particles (Satterfield, 1975). Although a certain amount of investigations have been carried out under elevated pressure and temperature (Wammes et al., 1991; Al-Dahhan and Dudukovic, 1994; Al-Dahhan et al., 1997), fluid dynamics in a fixed bed under supercritical condition has not been well investigated.

Supercritical fluids (SCFs) have many unique properties, which are not possessed by gases or liquids, such as excellent dissolving power, low viscosity, low surface tension, high diffusion coefficient, and high density (Liong et al., 1991). Among these properties, viscosity and diffusivity of SCFs are close to gas, while density of SCFs is close to liquid. These properties make SCFs appropriate to serve as multiphase reaction media (Subramaniam et al., 2002; Baiker, 1999), providing enhanced heat transfer and the potential for fast chemical reactions. As reaction media for diffusion-controlled reactions involve gaseous reagents such as hydrogen (Seki et al., 2008), SCFs are superior to the conventional liquid solvents for higher gas solubility and lower resistance to mass transfer. For example, Zhang et al. (2006) compared paraffin (inert media) and n-hexane (supercritical media) as methanol synthesis media on a Cu-based catalyst. They found that methanol synthesis with n-hexane at supercritical state could move the limitation of chemical reaction equilibrium (methanol concentration reaches 50%). Clearly, supercritical n-hexane played the role of reaction-separation coupling on the methanol synthesis process.

The advantages of heterogeneous catalytic reactions in supercritical media are very obvious, and experiments have also confirmed the importance of SCFs in industrial applications (Fan and Fujimoto, 1999; Yan et al., 1998; Zhang et al., 2006). However, current researches are mainly focusing on the exploration and discussion in chemistry, while the lack of researches in fluid flow and transfer processes is unfavorable for the industrialization of supercritical reaction processes. In TBRs, liquid physical properties and packing properties, besides fluid flow rate, also influence the

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pressure drop (Al-Dahhan et al., 1997), and larger particle size and lower liquid viscosity produce smaller pressure drop. Clearly, smaller size of catalyst gives rise to greater efficiency when solid catalyst is applied. As far as particle size is concerned, a contradiction appears between the pressure drop and the catalyst efficiency, but this contradiction can be, all or partially, alleviated by introducing SCFs into TBRs. SCFs own gas-like diffusive and viscosity, and liquid-like density, so flow of SCFs in TBRs is bound to produce smaller flow resistance, making the use of small particles in TBRs possible. The residence time distribution (RTD) and mean residence time (MRT) are powerful tools to evaluate the performance of fluid flow in reactors. Therefore, the main objective of this research is to investigate the performance of SCFs in a laboratory scale TBR with small particles when supercritical fluid and gas pass downward through the bed. Concretely, we would focus on two aspects: (1) RTD and MRT, and (2) pressure drop, so as to provide basic data and a theoretical basis for the design of TBRs with supercritical media. Meanwhile, subcritical fluids at elevated pressure and temperature were included for comparison.

Table 1
Bed dimensions, particle specification and operating conditions.

Reactor dimensions	
Total length	110 cm
Prepacking depth	25 cm
Bed length	70 cm
Support grid height	15 cm
Inner diameter	1.25 cm
Glass bead properties	
Shape	Sphere
Diameter: 1.32 mm	Bed porosity: 0.357
Diameter: 0.67 mm	Bed porosity: 0.355
Operating conditions	
Bed temperature	413–553 K
Total pressure	3.55–4.55 MPa
Superficial gas velocity	0.044–0.22 m/s for pressure drop 0.368–3.13 mm/s for RTD
Liquid (or SCF) mass flux	1.1–11.0 kg/(m^2 s) for pressure drop 0.371 kg/(m^2 s) for RTD

2. Material and methods

2.1. Experimental set-up

Experiments were carried out in a laboratory scale TBR. The TBR was made up of a stainless steel tube of 110 cm in length and 1.25 cm in inner diameter. Glass beads were used as packing material. The support grid for the packing was located 15 cm above the bottom flange. A well-packed bed was established by loading the reactor in batches of one-third of the total amount of packing material and by vibrating violently the column after loading each batch, until the height of the bed reached 70 cm. In the top of the reactor a 25 cm layer (prepacking) of 5.0 mm glass bead was set in order to get uniform radial liquid distribution over the reactor cross-section. At the center along the axial direction, a 3 mm (outer diameter) stainless tube was installed at the reactor; thus temperature at different positions of the bed could be measured with a thermocouple sensor. The reactor was externally heated with four electrical furnaces arranged along the reactor axial direction successively, and the bed temperature maintained within ± 3 K of the setpoint temperature by a controller connected to the electrical furnace. Pressure taps were drilled in the reactor top flange and bottom flange to measure the two-phase pressure drop through the reactor. The pressure drop was measured by a differential pressure transmitter (DPT), and stored simultaneously into a computer through an A/D card. Bed dimensions, particle specification and operating conditions are given in Table 1.

2.2. Experimental procedures

Nitrogen was used in our experiments; liquids were tap water and n-hexane. The liquid was delivered by metering pump to the reactor at the top of the reactor, and the liquid mass flux was adjusted by the pump head setting. The gas, which was supplied from a high-pressure gas buffer, flowed through calibrated mass flow controller (MFC) to measure its feed rate. Before the liquid and gas were delivered to the reactor, they were heated in the preheater with another electrical furnace. The temperature of fluid at the preheater outlet was automatically adjusted to the desired temperature by a control unit. Exiting solutions (gas and liquid) from the reactor was firstly cooled, and subsequently went through the gas–liquid separator. In the top flange of the separator, stainless steel mesh demister was placed to trap the liquid mist from the effluent gas stream. Pressure indicator and safety valve were mounted to prevent pressure accumulating in the gas and liquid delivery and exit stream. Check valve was located in gas and liquid branch to assure the flow in one direction.

RTD experiments were carried out with the tracer response method. n-dodecane was used as tracer and was introduced to the reactor as a pulse through the valve mounted on the top of the trickle-bed reactor. In all RTD experiments, glass beads were 1.32 mm in diameter; the fluids were N_2 and n-hexane. At the beginning of each experiment, the reactor was filled with n-hexane at the operating conditions (3.55 MPa, 483 K or 513 K) for about an hour to pre-wet the bed; then N_2 and n-hexane were simultaneously introduced into the reactor, and the flow rates of gas and n-hexane were adjusted to the desired values. After an hour, about 0.5 ml tracer was rapidly injected into the reactor; at the same time, sampling with a regular time interval was conducted at the outlet (next to the cooler). Tracer concentration was determined with a gas chromatograph (GC) equipped with a capillary column (AT PEG 20M) of 30 m in length (0.25 mm i.d., 0.5 μm film thickness) and a flame ionization detector (FID). The column temperature was kept constant at 453 K, while the temperatures at the injector and the detector were both set at 493 K; N_2 was used as the carrier gas. Chromatographic data were collected by a N2000 Chromatography data acquisition system. In order to eliminate the effect of cooler and other parts, blank experiments, i.e. without the glass beads, were run (Ring and Missen, 1991).

In all experiments of determining pressure drop, the reactor was operated in high interaction regime at high gas and liquid flow rate for about 30 min after the bed was heated up to 10 K above the desired temperature. This pretreatment process was to achieve perfect bed prewetting and to prevent hysteresis effects. Subsequently, we reduced the gas and liquid flow rate and temperature to the desired level. When reactor pressure, temperature and the fluid flux reached pre-set values and kept steady for more than 15 min, we could collect the instantaneous pressure drop. Sampling lasted about 5 min with a frequency of 10 Hz. After the data acquisition finished, operational parameters, such as temperature or fluid flux, were adjusted to another desired level. It took a long time for the trickle-bed to reach the new state, and the interval between two samplings was about 45 min. Because of the considerable fluctuation of pressure drop in the high interaction regime, the bed pressure drop was defined as

$$\frac{\Delta P}{Z} = \frac{1}{n}\sum_{i-1}^{n}\frac{\Delta P_i}{Z} \quad (1)$$

where Z was the bed height, and i was the sampling number.