Influence of heat exchanges and of temperature profile for carbon nanotube synthesis in a continuous rotary reactor

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Abstract

The influence of the reaction exothermicity has been taken into account for the modeling of a continuous inclined mobile-bed rotating reactor for carbon nanotube synthesis by the CCVD method using ethylene as carbon source. The modeling of the continuous reactor was performed according to the reaction chemical engineering approach which consists in studying the four factors governing the reactor, i.e. geometric, hydrodynamic, physical and physico-chemical factors [1]. So the reactor equations have been written by applying the co-current plug-flow hypothesis and by taking the true kinetic equation and the sigmoid catalytic deactivation into account [2]. The four reactor equations correspond to the three mass balances and to the heat balance.

The optimal temperature to maximize the productivity and to avoid the formation of soot and tars is equal to 700°C with ethylene [3, 4]. In small scale reactors, the heat exchange between the carbon nanotube growing bed and the atmosphere of the furnace surrounding the reactor is efficient enough to evacuate the heat released by the reaction and to keep the temperature constant along the reactor. However, for higher production capacity reactors, the global heat released by reaction increases, and the heat exchange has to be efficient enough to evacuate the heat released by the reaction. Otherwise, one may observe a runaway phenomenon. So the heat released by reaction influences the temperature profile through the reactor and heat exchanges have to be taken into account to model the axial temperature profile.

The model has been validated with data obtained on two industrial reactors equipped with heating systems belonging several distinct heating zones with the same length providing an adequate control of the temperature in the reactor. To avoid a too high reaction speed, possibly leading to excessive heat release and to hot point responsible of cracking of ethylene and of reactor fouling by tars and soot deposition in the first reactor sections, the feed temperature of the reacting gas has to be fixed at a value lower or equal to 650°C. Indeed, Fig. 1 highlights the temperature profiles for initial temperatures equal to 650°C and 700°C for a given experimental set. When the initial gas temperature is equal to 700°C, the heat release leads to a significant temperature increase beyond 700°C, leading to a great deposition of soot and tars. Fig. 1 shows the corresponding temperature profile, which is continuously increasing and tends towards an adiabatic profile.

Furthermore, the model shows that the temperature profile along the reactor has to be as close as possible of the temperature profile of an isothermal reactor at 700°C (Fig.2). This temperature profile can be reached with several heating zones (at least four heating zones) and with an initial temperature at the inlet of the reactor smaller than 700°C due to the exothermicity of the reaction. This result is in agreement with experimental data obtained with the two industrial reactors.

Several articles in the literature show that the fluidized-bed reactor works correctly and produce CNT of good quality [5-7]. According to some references, the fluidized-bed reactor is the only one able to produce CNTs continuously in a large-scale and has already been adopted worldwide for the commercial production of CNTs, because compared with moving-bed reactor, the fluidized-bed reactor has excellent heat and mass transfer properties and good mixing behavior. However, the residence time of each catalyst particle is not constant in a fluidized-bed reactor, leading to an inhomogeneous quality of produced CNTs. The present article shows that by imposing an adequate temperature at the inlet of the reactor and by controlling the temperature of the heating zones in order to regulate heat exchanges between the CNT growing bed and the atmosphere of the heating zones through the reactor wall, the temperature profile along an industrial continuous mobile-bed reactor is almost isotherm and this kind of reactor is very well adapted to continuously produce CNTs of homogeneous quality at a large-scale.

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Figures

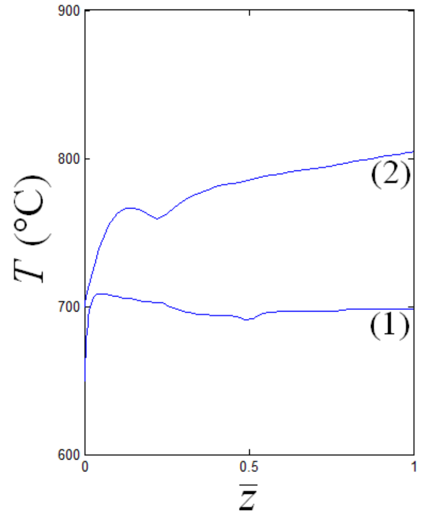

Fig. 1. Modeled temperature profiles in a reactor with four heating zones for a given experimental set: (1) for an initial temperature equal to 650°C; (2) for an initial temperature equal to 700°C).

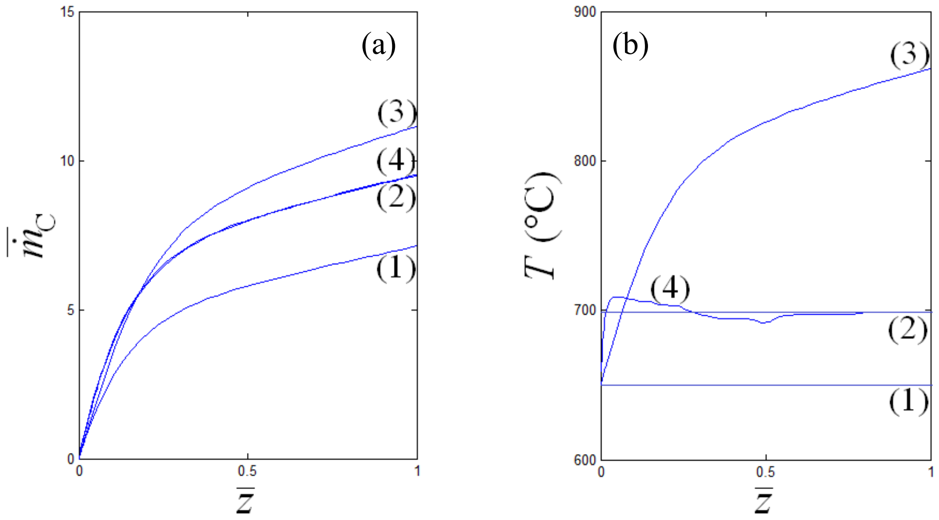

Fig. 2. Modeled profiles for a given experimental set: (a) specific productivity and (b) temperature (1) profiles for an isothermal reactor at 650°C; (2) profiles for an isothermal reactor at 700°C; (3) profiles for an adiabatic reactor and (4) profiles for a reactor with heat exchanges (four heating zones with the same length).