



Research article

Synthesis of carbon nanotubes from conventional biomass-based gasification gas

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ABSTRACT

The gas product which synthesized from the biomass-based gasification process is a kind of rich carbon source gas. To establish the high-value applications, the synthesis process of carbon nanotubes (CNTs) from biomass-based gasification gas is established in this study. This study focused on the CNTs production process from the mixture of CO and CH₄, which were primary components of biomass pyrolysis/gasification gas, in a thermogravimetric and a fluidized bed. The reaction temperature and the partial pressure of the essential role of the mixture gas were investigated. Meanwhile, in the fluidized bed, results of the decomposition of mixture gas (CO/CH₄) were compared with the results by pure gas (CH₄ decomposition process and CO disproportionation process). Results showed that the initial temperature for carbon weight gain increased in the mixture gas decomposition process was lower than that of the pure CH₄ decomposition process in the TG reactor. In the fluidized bed, the conversions of CO and CH₄ were promoted in the mixture gas decomposition process. CO and CH₄ played a synergistic role with the H₂ as the medium in the CO/CH₄ decomposition process. With the increase of CO/CH₄ partial pressure ratio, the yield and quality of CNTs increased significantly. The CNTs produced from CO/CH₄ were longer and smoother than that of CH₄ and CO decomposition. When the partial pressure ratio of CO/CH₄ up to 2, the yield of carbon weight gain was eight times than that of same partial pressure of CH₄ decomposition. Therefore, it is feasible for the decomposition of biomass-based gasification gas for the CNTs formation process.

1. Introduction

Biomass pyrolysis/gasification process plays a significant role in the energy fuel system due to the convention of the low-value feedstocks to the high-quality combustible gases which consist mainly of H₂, CO, CH₄, CO₂, and N₂ in various proportions [1–3]. The typical application of the gas products is directly burning used with electricity generation or turning into liquid transportation fuels. However, is there any other method by using the gases produced from biomass pyrolysis/gasification process for a high-value application? From the component view of the gas, CO, CO₂, and CH₄, as the rich carbon source gas, can be used for the high-value solid carbon material preparation process.

Carbon nanotubes (CNTs) exhibited the high mechanical strength, excellent thermal conductivity and electronic characteristics [4] which are applied widely in the energy and environmental shields and viewed as the target materials in this study. According to the literature, CH₄

decomposition [5,6], CO disproportionation [7,8] and methane reforming [9,10] processes for CNTs synthesis were drawn much attention recently. To expand the carbon source gas field, we established a novel approach for CNTs produced from the conventional biomass-based gasification process. There were few researchers considered the composition of the pyrolysis/gasification gas for CNTs synthesis. Maghrebi et al. [11] found that the additional gas with oxygen element can effectively inhibit the deactivation of the catalyst in the carbon mixture gases. Nishii [12] synthesized a large number of CNTs with the coal gasification syngas (CO and H₂) as the carbon source gas at 800–900 °C. CNTs production considered by the component of CO and CH₄ both simultaneously has hardly any research; therefore, this research focused on the component with CO and CH₄ for CNTs production from conventional biomass-based gasification process.

In this study, commercial NiMg/Al₂O₃ (atomic ratio Ni/Mg = 1/1) catalysts were used for determining the decomposition characteristic of

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the mixture gas of CO and CH₄. A thermogravimetric (TG) analyzer was adopted for obtaining the reaction temperature range and carbon deposition feature. The catalytic decomposition processes of carbon source gas were created in a fluidized bed reactor. In the fluidized bed, the synthesis process can be reached maximization procedure on the catalyst surface which was limited in the TG reactor. Meanwhile, the essential operation parameters were measured to master the mechanism during a decomposition process. Gas components (CH₄, CO, and CO/CH₄), bed temperature (450°C, 550 °C, and 650 °C) and various partial pressure of the gas (0.1 atm, 0.2 atm, and 0.4 atm) were investigated to determine the characteristic of carbon formation in the fluidized bed. The carbon products were confirmed as nanotubes through the measurements of the scanning electron microscopy (SEM), transmission electron microscope (TEM) and Raman spectroscopy.

2. Experiment

2.1. Activity tests and CNTs synthesis process

The activity tests over the NiMg/Al₂O₃ catalyst for the CO/CH₄ mixture gases were performed in a thermogravimetric analyzer (TG, WCT-2A). Before the reaction, to avoid spatial limitations, 5 mg reduced catalyst (by H₂ in 30 min) samples were loaded into the crucible and deposited in the furnace. Typically, a mixture gas of carbon source gas and N₂ with a total flow of 70 mL/min was explored as the reaction gas from room temperature to 800 °C with the rate of 10 °C/min at atmospheric pressure. The N₂ was a carrier gas to balance the total gas flow. The partial pressure ratio of CH₄ was as a constant of 0.1 atm. The effect of the partial pressure ratio of CO/CH₄ on the final carbon deposit rate was investigated. The weight gain changes during the reaction were measured consecutively.

The CNTs synthesis experimental system was a lab-scaled fluidized

bed as shown in Fig. 1. The reactor was made of a quartz tube with a total length of 1250 mm and an internal diameter of 30 mm. The distributor with lots of uniform distribution pores for the high resistance force was plated in the middle of the fluidized bed. In each experiment, a certain amount of catalysts (kept the same ratio of carbon source to catalyst equal to 4.41 L·h⁻¹·g⁻¹, which was the best condition for carbon source decomposition) were located upon the distributor before the reaction started. Firstly, the temperature was heated from room temperature to 500 °C with a rate of 15 °C/min in an N₂ atmosphere, then the gas translated into the mixture of H₂/N₂ gas for 30 min at 500 °C to reduce the catalyst from the oxidation state to the reduced state. Secondly, the mixture gas was switched to the pure N₂. Meanwhile, after warming or cooling to the preset reaction temperature, the carbon source gas was introduced and maintained 60 min. The generated gaseous products were passed through the filter device and dryer, then analyzed by the MRU gas analyzer with the data recording consecutively. The solid products were weighted after cooling in the N₂ atmosphere for 30 min.

2.2. Data analysis

In the carbon source decomposition processes, carbon sources (CH₄ or CO) must be “cracked” or broken into the C–H links or C=O links to produce the carbon products. The performance of this operation evaluated by using the conversion rate as follows:

$$X_{i,t} = (F_{in,i,t} - F_{out,i,t})/F_{in,i,t} \times 100 \quad (1)$$

where *i* represents CH₄ or CO, *F* is the amount (mL/min) of CH₄ or CO with time, the subscript of *in* or *out* is the input amount or output amount.

The yield of hydrogen (H₂ yield, expressed as *Y*_{H₂}) was determined as followed:

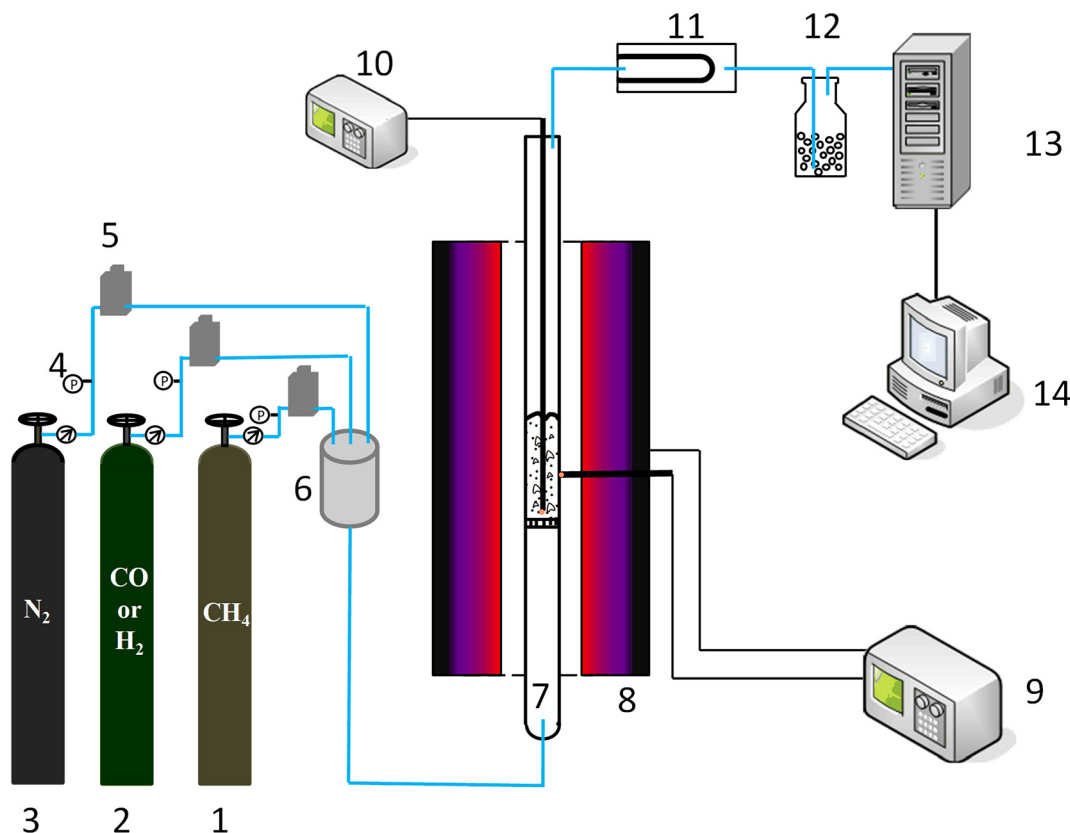


Fig. 1. Schematic of fluidized bed reactor. 1. Methane; 2. CO or H₂; 3. N₂; 4. Regulating valve; 5. Mass flow controller; 6. Gas mixer; 7. Quartz tube reactor; 8. Electric heating furnace; 9. Heating furnace temperature control device; 10. Thermocouple; 11. Filter device; 12. Dryer; 13. Gas analyzer; 14. Computer.

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