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# Synthesis mechanism of carbon nanotube fibers using reactor design principles

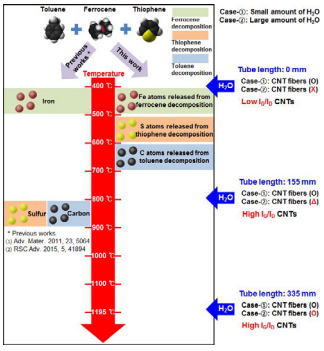
Sung-Hyun Lee [a,b,*], Hye-Rim Kim [b], Haemin Lee [b], Jinwoo Lee [b], Cheol-Hun Lee [b], Jaegeun Lee [c], Junbeom Park [a], Kun-Hong Lee [b,*]

[a] Carbon Composite Materials Research Center, Korea Institute of Science and Technology, 92, Chudong-ro, Bongdong-eup, Wanju-gun, Jeollabuk do 565-905, South Korea
[b] Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), San 31, Hyoja-Dong, Nam-Gu, Pohang, Gyungbuk 790-784, South Korea
[c] Department of Industrial Engineering, University of Pittsburgh, 3700 O'Hara Street, Pittsburgh, PA 15261, USA

## HIGHLIGHTS

- Quality of the CNT fibers and continuity of the synthesis of CNT fibers were improved by applying reactor design principles.
- Identification of decomposition temperature and reaction sequence of chemicals in direct spinning process.
- Understanding on the effect of water on the decomposition of chemicals in the synthesis of CNT fibers.
- Increase of the quality of CNT fiber by controlling the injection position of water in the vertical reactor.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The direct spinning process is a useful method for continuously synthesizing carbon nanotube (CNT) fibers. A reactor should be designed based on reactor design principles in order to study the synthesis mechanism and mass production of CNT fibers. The internal temperature in a continuous flow reactor depends on the length of the reactor, and because the temperatures required for the decomposition of various feedstocks differ, each feedstock is decomposed at a different point in the reactor. Here, we report that high-quality CNT fibers were continuously synthesized by water injection at temperatures above the catalyst-forming range during the direct spinning process, as determined by the decomposition temperatures of the feedstocks. The decomposition temperatures of the feedstock materials were measured. Thiophene and toluene decomposed at 500–600 °C and 600–700 °C, respectively, and these temperatures were lower than those reported in the literature. The quality of the CNT fibers was improved by injecting water into zones with temperatures that exceeded the decomposition temperatures of the feedstocks in the reactor. Oxygen containing functional groups formed less often on the CNT surfaces, further improving the quality of CNT fibers. Moreover, the CNT fibers were continuously synthesized, even if excess water were injected.



## 1. Introduction

Carbon nanotubes (CNTs) are potentially useful in various industrial fields because of their excellent properties, including their high tensile strength, thermal conductivity, and electrical

* Corresponding authors at: Carbon Composite Materials Research Center, Korea Institute of Science and Technology, 92, Chudong-ro, Bongdong-eup, Wanju-gun, Jeollabuk do 565-905, South Korea (S.-H. Lee).
*E-mail addresses:* sunghyun.lee@kist.re.kr (S.-H. Lee), ce20047@postech.ac.kr (K.-H. Lee).

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conductivity (Baughman et al., 2002; Endo et al., 2008). CNT fibers formed by twisting many CNTs together have attracted attention as materials with widespread applicability (Mora et al., 2009; Foroughi et al., 2011; Dalton et al., 2003; Zhao et al., 2010; Zhu et al., 2010). The direct spinning method, which is one method for manufacturing CNT fibers, is industrially useful because CNT synthesis and fiber formation occur simultaneously in a single reactor (Li et al., 2004). CNT fibers with good properties can be produced through direct spinning (Koziol et al., 2007); however, the synthetic mechanism underlying the direct spinning process is not yet fully understood because all feedstocks are injected simultaneously. Catalyst formation and CNT synthesis, therefore, occur very rapidly in the reactor. Previously, the CNT fiber synthesis conditions were optimized in the direct spinning method by varying the concentrations of the injected feedstock (the inputs) and monitoring the properties of the synthesized products (the outputs). This trial and error method required considerable time and effort to optimize the synthesis conditions because it was difficult to predict and determine the reaction order and type inside the reactor. An in-depth study of the internal reaction process is needed to clarify the sequence and type of reactions taking place inside the reactor. Since CNT synthesis is closely related to the decomposition of the injected precursor, it is important to control the temperature distribution inside the reactor and the injection position of the material.

The injection tube length and the temperature profile inside the reactor were obtained based on reactor design principles. The continuity and quality of the CNT fiber synthesis could be improved by designing a reactor based on the design principles Fig. 1). When optimizing the synthesis conditions of the CNT fibers, the temperature profile inside the reactor plays an important role. The temperature gradually increased with the length of the reactor, and the decomposition temperatures differed for each feed material, enabling the continuous synthesis of CNT fibers. The synthesis of CNT fibers could be divided into a catalyst formation step and a CNT synthesis step (Lee et al., 2017). In the catalyst formation step, the catalyst precursor was first decomposed to form the catalyst particles. Carbon atoms generated from decomposition of the carbon precursor were then supplied to the catalyst particles to synthesize the CNTs. If the temperature did not change with the length of the reactor, the catalyst precursor and the carbon precursor decomposed simultaneously to limit the synthesis of CNT fibers. The catalyst particles were deactivated by contact with the carbon atoms prior to catalyst growth to the size required for CNT synthesis. Therefore, it is important to understand the temperature profile inside the reactor and the decomposition temperatures of the feed materials (Fig. 1(b) and (c)). Previous studies of the positions at which materials decomposed inside the reactor based on the temperature profile were published by our group (Lee et al., 2015). These reports did not consider that the decomposition temperatures of the materials could change with the experimental conditions (see, for example, studies of thiophene (Zaera et al., 1987; Bajus et al., 1981) Developing a model to describe the decomposition temperatures of feed materials under conditions similar to those used to synthesize CNT fibers would be important to studies of the synthesis mechanism.

Reactors designed using reactor design principles can improve the synthesis of high-quality CNT fibers. In a conventional synthesis method, all feed materials are simultaneously injected into a single reactor, and the position at which the injected material influenced the reaction was determined by the internal reactor temperature. In this case, the selection of the materials was limited. Injecting materials at a specific location and temperature within the reactor could tune the synthetic reaction processes and assist a mechanistic study (Fig. 1(a) and (b)).

In this study, the quality and continuity of the CNT fiber synthesis were improved using a reactor designed based on reactor design principles. The practical decomposition temperatures of the feed materials were determined, and the catalyst formation and CNT synthesis regions were distinguished by distinct temperature profiles inside the reactor. The decomposition temperatures of the feed materials differed from those reported previously. The quality of the CNT fibers was improved by injecting water at a specific position inside the reactor. Moreover, the CNT fibers composed of CNTs with a clean surface were continuously synthesized, even in the presence of excess water. These results were obtained from a systematic analysis of the direct spinning process, which reveals the mechanisms underlying CNT fiber synthesis and ultimately contributes to the industrialization of CNT fibers.

## 2. Experimental

### 2.1. Measurement of the decomposition temperatures of thiophene and toluene

Experiments to confirm the decomposition temperatures of thiophene and toluene were performed using a horizontal reactor.

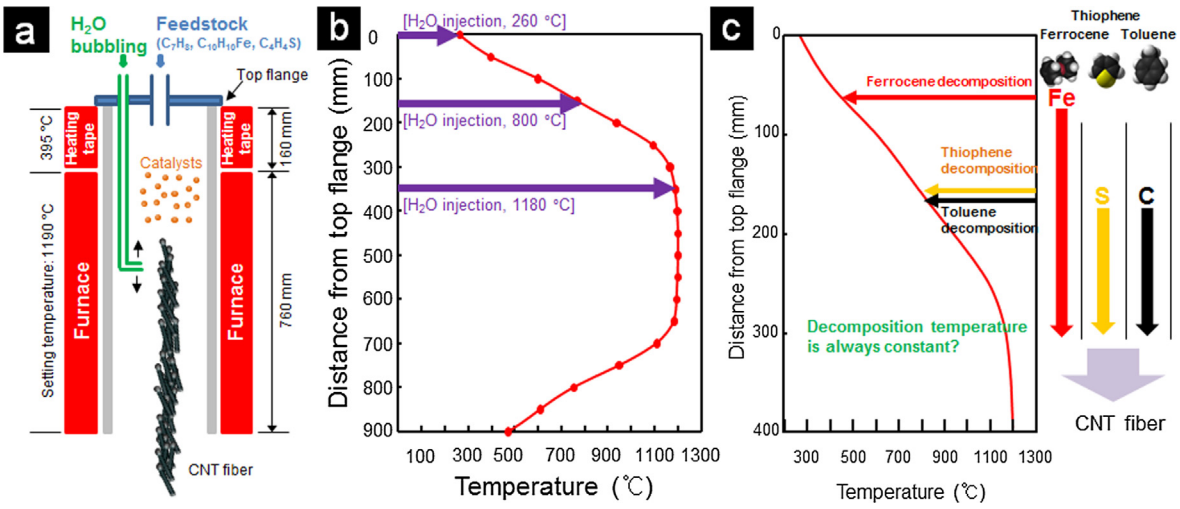


**Fig. 1.** Fabrication of the CNT fibers based on reactor design principles. (a) Schematic illustration of a vertical reactor using the water injection tube. (b) Temperature profile inside the vertical reactor. (c) The decomposition points of the feed materials inside the reactor based on the decomposition temperature reported previously.