Chemical Engineering Journal 144 (2008) 267–269

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Short communication

A comparison of carbon nanotube synthesis in fixed and fluidised bed reactors

Chee Howe See*, Andrew T. Harris

Laboratory for Sustainable Technology, School of Chemical and Biomolecular Engineering, University of Sydney, NSW 2006, Australia

ARTICLE INFO

Article history:
Received 6 March 2008
Received in revised form 30 May 2008
Accepted 4 June 2008

Keywords:
Fixed bed
Fluidised bed
Chemical vapour deposition
Carbon nanotubes

ABSTRACT

A comparison of carbon yield reported for both fixed and fluidised bed reactors reported in the literature demonstrates that low yields are not a limitation of a fluidised bed system.

The unique properties of carbon nanotubes (CNTs) make them suitable for use in a wide range of applications, including biology and medicine, as polymeric additives and in energy devices. However, the commercial uptake of CNTs has been slow because of insufficient production capacity and high pricing which has resulted from restricted supply. Unless CNTs are priced at commercially acceptable levels, market forecasts of “US$ 700 million by 2007 [1]” and “US$ 3.9 billion by 2010 [2]” are unlikely to be realised. Most recently, BCC research reported that revenue from sales of CNTs in 2006 was US$ 50.9 million and their consequent projections for 2007 were drastically reduced from US$ 700 million to US$ 79.1 million [3].

A likely route to high throughput CNT production is via chemical vapour deposition (CVD) because of its comparative simplicity, ease of control and low cost [4]. CNT synthesis via CVD is typically performed over transition metal catalysts (e.g. Fe, Ni, Co) supported on a substrate (e.g. alumina, silica, zeolites), although the reaction can be realised in both homogeneous and heterogeneous systems [5]. Fixed bed CVD reactors of varying configuration have been intensively studied for CNT synthesis. Despite the exceptional yields reported, e.g. 45 times an initial catalyst weight of 50 mg [6], the scale-up of fixed bed systems is non-trivial because of heat and mass transfer limitations. For CNT synthesis in a fixed bed, the mass of carbon deposited is a function of mass transport (e.g. diffusion) to active catalyst sites; as a result, the mass yield of carbon per unit weight of catalyst is related to the reactor geometry rather than the quantity of catalyst present. Reactor geometry in large-scale, fixed bed industrial processes plays a less significant role in product separation where the products are either a liquid or gas, e.g. alcohol dehydration, Beckmann rearrangement, paraffin isomerisation, cracking and alkylation processes [7]. In CNT synthesis however, the desired product is a solid which coats the catalyst particles and can act to retard further heat and mass transfer.

In the literature, most studies on the synthesis of CNTs in fixed beds make use of small quantities of catalyst (<1 g) in an effort to minimise these limitations. Larger catalyst beds require larger surface areas to obtain good yields. For example, Zeng et al. [8] reported that by doubling the catalyst surface area (by spreading the catalyst between two ceramic boats rather than one) the carbon yield increased by a factor of 3 when all other variables were held constant. In practise, this means that catalysts within a 3D structure effectively result in carbon yields equivalent to 2D structures with the same available surface area. Process optimisation at large-scale therefore requires the elimination of heat and mass transfer limitations, e.g. by using thin catalyst films, small particles and/or porous materials, to increase the gas–solid interfacial area.

By contrast, in a fluidised bed, stagnant film formation at the solid surface, which hinders heat and mass transfer, can be significantly reduced because of the vastly improved gas–solid mixing which is inherent in well-designed systems. Indeed, heat and mass transfer under ideal fluidisation conditions is non-limiting [9]. The good mixing between gas and solid particles in a fluidised bed provides access to active catalyst sites even in 3D geometries. In addition, fluidised beds have been shown to provide sufficient space for CNT growth when compared with fixed bed reactors [10]. These advantages have resulted in the use of fluidised beds in several commercial CNT pilot plants, e.g. Arkema^{TM} (France, up to 30 tons/year MWCNTs), Southwest Nanotechnologies (USA, kg/day SWCNTs), Baytubes (Germany, 30 tons/year MWCNTs), although

---

* Corresponding author. Tel.: +61 2 9036 6244; fax: +61 2 9351 2854.
E-mail address: c.see@usyd.edu.au (C.H. See).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.06.002

very little information is available in the public domain or scientific literature about these processes [11,12]. In particular, data on yield and fluidisation conditions [13], essential for understanding scale-up, are lacking.

Consequently, we feel it is misleading to discount results from laboratory-scale fluidised bed research because of 'low' yields since these cannot be directly compared with results from fixed beds, without the inclusion of a scale-up factor (to account for heat and mass transfer limitations). In addition, most laboratory fluidised bed systems are operated in batch mode and are further constrained by design to processing micron size substrates (typically >100 μm). The adoption of circulating (fast) fluidised beds (CFBs) currently used in state of the art metallurgical, chemical and energy processes, will move to eliminate these constraints from both laboratory- and industrial-scale systems. In a well-designed, continuous fluidised bed, the carbon yield, defined as the total mass of carbon deposited per unit mass of catalyst metal, is likely to increase with the use of smaller sized powders (<10 μm) or more porous substrate materials, due to the increased surface area (to volume ratio).

Our objective in this work is to address the concerns of some CNT researchers on the equivalence of the CVD reaction in fixed and fluidised beds, specifically related to 'low' apparent yields and batch operation reported in the majority of fluidised bed studies. We feel the latter is inevitable in laboratory-scale research, both in terms of economics and viability, e.g. it is simply not cost effective to process tens of kilograms of catalyst to test a single unknown condition using a fluidised bed. Consequently, most laboratories conduct parametric studies in batch mode before further optimisation in continuous pilot plants, e.g. Baytubes (Germany) [14]. Unfortunately, the comparative novelty of CNT synthesis in fluidised beds has resulted in a lack of primary results in the open literature. We feel this is probably due to the fact that it is easier to set up and operate a fixed bed reactor with a few grams of catalyst than a fluidised bed. Despite this, the use of fluidised beds in industrial trials is rather telling, as these operators have presumably chosen fluidised beds because they are the most cost effective, scaleable alternative.

To address the issue of 'low' carbon yields cited by some researchers, we have plotted the carbon yield obtained from both types of reactor in Fig. 1 (the data is taken from supporting information, Tables 1 and 2). These data suggest that there is a dearth of useful information on the fluidised bed synthesis of CNTs, but where this information is reported, the yields are consistent with those observed in fixed beds. Fluidised beds appear to have the additional advantage that similar carbon yields are maintained at higher catalyst mass loadings and are therefore inherently better suited to high throughout processing.

Finally, we wish to briefly comment on some of the results and assumptions reported in the literature. For example, the promising carbon yields reported by Zhao et al. [15] and Liu et al. [16] (18 g/g catalyst and 22 g/g catalyst, respectively) are confusing because the overall conversion based on the total carbon feed appears to exceed 100%. It is also erroneous in our opinion, to suggest that the CNT yield is equivalent to carbon yield, unless of course the selectivity is 100%, which is difficult to verify experimentally. The verification of 100% selectivity (e.g. Perez-Mendoza et al. [17]) must be substantiated using quantitative characterisation tools other than SEM/TEM imaging, as discussed by Itkis et al. [18] We are further concerned by the lack of yield information reported in the majority of fluidised bed studies, particularly because the purpose of using these systems is to (ultimately) achieve large-scale synthesis. Furthermore, while Liu et al. [16] and Mauron et al. [19] report the use of fluidised beds, the low bed mass employed (0.1 g and 1.5 g, respectively) in these studies is problematic, because the quantity of powder used suggests that electrostatic effects would have been dominant [20]. The 1.5 g of powder used by Mauron et al. in a 30 mm would have a bed height of ≈2 mm [12], which is likely unstable and will not allow a full fluidisation profile to develop.

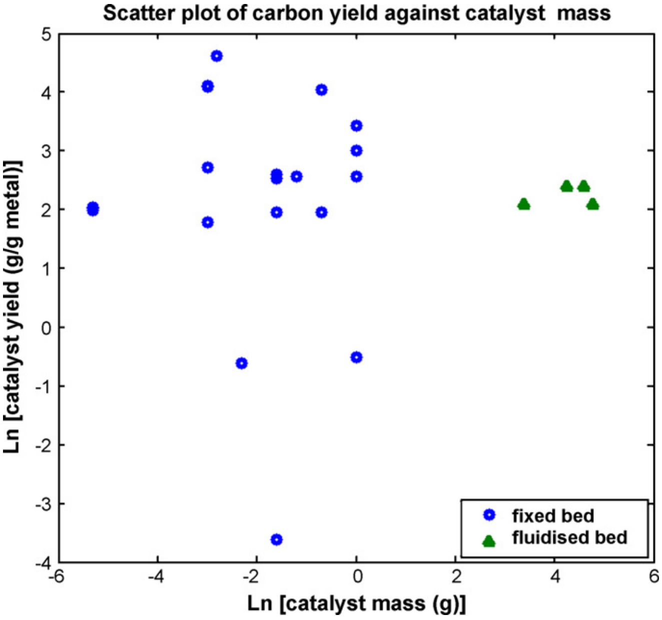

Fig. 1. Scatter plot of carbon yield as a function of catalyst mass showing that the CNT yield in published fluidised bed studies is consistent with those in fixed bed studies, even at high catalyst bed loadings. The data is tabulated in Tables 1 and 2 in the supporting information.

In conclusion, we have shown that the carbon yields obtained in fixed and fluidised bed reactors reported in the literature are consistent, but that fluidised bed reactors have the advantage of being able to accommodate a greater quantity of catalyst and therefore higher throughputs are achievable. We also suggest that further evidence of the suitability of fluidised beds is provided by the use of this technology in industrial-scale plants for CNT synthesis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2008.06.002.

References

[1] BCC, Carbon Nanotubes: Worldwide Status and Outlook—Applications, Applied Industries, Production, R&D and Commercial Implications, Fuji-Keizai, USA, 2002.
[2] Cientifica, Carbon Nanotube Global Production, Cientifica, UK, 2004.
[3] BCC, Carbon nanotube use in composites predicted to soar, Addit. Polym. 2007 (6) (2007) 9.
[4] K.P. de Jong, J.W. Geus, Carbon nanofibers: catalytic synthesis and applications, Catal. Rev. 42 (4) (2000) 481–510.
[5] C.H. See, A.T. Harris, $CaCO_3$ supported Co–Fe catalysts for carbon nanotube synthesis in fluidised bed reactors, AIChE J. 54 (2008) 657–664.
[6] Y. Li, X.B. Zhang, X.Y. Tao, J.M. Xu, W.Z. Huang, J.H. Luo, et al., Mass production of high-quality multi-walled carbon nanotube bundles on a Ni/Mo/MgO catalyst, Carbon 43 (2) (2005) 295.
[7] G. Busca, Acid catalysts in industrial hydrocarbon chemistry, Chem. Rev. 107 (11) (2007) 5366–5410.
[8] X. Zeng, X. Sun, G. Cheng, X. Yan, X. Xu, Production of multi-wall carbon nanotubes on a large scale, Physica B 323 (1–4) (2002) 330–332.
[9] M. Perez-Cabero, I. Rodriguez-Ramos, A. Guerrero-Ruiz, Characterization of carbon nanotubes and carbon nanofibers prepared by catalytic decomposition of acetylene in a fluidized bed reactor, J. Catal. 215 (2) (2003) 305–316.
[10] W. Qian, F. Wei, Z. Wang, T. Liu, H. Yu, G. Luo, et al., Production of carbon nanotubes in a packed bed and a fluidised bed, AIChE J. 49 (3) (2003) 619–625.
[11] A.M. Thayer, Carbon nanotubes by the metric ton, Chem. Eng. News 85 (46) (2007) 29–35.

[12] C.H. See, A.T. Harris, A review of carbon nanotube synthesis via fluidized-bed chemical vapor deposition, Ind. Eng. Chem. Res. 46 (4) (2007) 997–1012.

[13] H. Yu, Q. Zhang, F. Wei, W. Qian, G. Luo, Agglomerated CNTs synthesized in a fluidized bed reactor: agglomerate structure and formation mechanism, Carbon 41 (14) (2003) 2855–2863.

[14] M. Bierdel, S. Buchholz, V. Michele, L. Mleczko, R. Rudolf, M. Voetz, et al., Industrial production of multiwalled carbon nanotubes, Phys. Stat. Sol. (b) 244 (11) (2007) 3939–3943.

[15] N. Zhao, C. He, Z. Jiang, J. Li, Y. Li, Fabrication and growth mechanism of carbon nanotubes by catalytic chemical vapor deposition, Mater. Lett. 60 (2) (2006) 159.

[16] B.C. Liu, L.Z. Gao, Q. Liang, S.H. Tang, M.Z. Qu, Z.L. Yu, A study on carbon nanotubes prepared from catalytic decomposition of C_2H_2 or CH_4 over the pre-reduced $LaCoO_3$ perovskite precursor, Catal. Lett. 71 (3/4) (2001) 225–228.

[17] M. Perez-Mendoza, C. Valles, W.K. Maser, M.T. Martinez, S. Langlois, J.L. Sauvajol, et al., Ni-Y/Mo catalyst for the large-scale CVD production of multi-wall carbon nanotubes, Carbon 43 (14) (2005) 3034–3037.

[18] M.E. Itkis, D.E. Perea, S. Niyogi, S.M. Rickard, M.A. Hamon, H. Hu, et al., Purity evaluation of as-prepared single-walled carbon nanotube soot by use of solution-phase near-IR spectroscopy, Nano Lett. 3 (3) (2003) 309–314.

[19] P. Mauron, C. Emmenegger, P. Sudan, P. Wenger, S. Rentsch, A. Zuttel, Fluidised-bed CVD synthesis of carbon nanotubes on Fe_2O_3/MgO, Diamond Relat. Mater. 12 (3–7) (2003) 780–785.

[20] J. Ciborowski, A. Wlodarski, On electrostatic effects in fluidized beds, Chem. Eng. Sci. 17 (1) (1962) 23–32.