

Customization for Current Market Applications of the Carbon Nanotubes Produced by PNNL's Regenerable Catalytic Pyrolysis (ReCaP) for Scaled Hydrogen Production

September 2023

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Abstract

Here, we demonstrated the Regenerative Catalytic Pyrolysis (ReCaP) process that generates carbon dioxide-free hydrogen (CO_2 -free H_2) from inexpensive and domestically abundant natural gas (NG), while simultaneously producing H_2 at net production cost of \$1.0/kg through the sale of valuable carbon nanotube (CNT) co-product. The specific goal of this project is to 1) scale up the production of CNT, 2) correlate the properties of the CNT with the reaction conditions, 3) perform a techno-economic analysis to obtain minimum selling price of H_2 and CNT, and 4) identify industrial partners interested in the CNT co-product.

Summary

In this study, we investigated the scale-up of the ReCaP process using fluidized-bed reactor technology to increase the catalyst longevity and carbon nanotube (CNT) production from the catalyst bed. We evaluated how reaction conditions such as catalyst loading, space velocity, temperature, and gas composition affected the catalyst performance and CNT product. We increased the carbon production from 5 to 450 g and identified correlations between the properties of the CNTs and reaction conditions. A preliminary techno-economic analysis reveals that the DOE's Hydrogen Earthshot Goal of \$1/kg H₂ can be accomplished by the sale of the CNT at \$1.75/kg, which is two order of magnitude lower cost than comparable CNT products in the market. Industrial partners interested in this technology tested the properties of the CNTs and provided additional research and optimization direction.

Acknowledgments

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Acronyms and Abbreviations

ReCaP: Regenerative Catalytic Pyrolysis

CO₂-free H₂: carbon dioxide-free hydrogen

NG: natural gas

CNT: carbon nanotube

MWCNT: multiwalled carbon nanotube

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1.0 Introduction

PNNL's ReCaP process generates CO₂-free H₂ from inexpensive and domestically abundant NG, while simultaneously reducing H₂'s net production cost to \$1.0/kg through the sale of valuable crystalline solid CNT co-product¹⁻⁵. This assumes that a suitable carbon markets exist or can be developed for the produced CNTs. PNNL is actively engaged in a R&D effort - with direct funding from Southern California Gas Company - to explore the development of new market applications for produced CNTs. This includes research aimed at developing composites for use in i) thermoplastics, ii) automotive, iii) cement, iv) steel, and v) battery applications. If successful the direct-funded work would lay the groundwork for identifying multiple, large volume markets for the produced solid carbon, with its value dictating the economics of the process, simultaneously producing clean H₂ as an inexpensive byproduct.

While promising these development efforts will take time. Thus, the team seeks to identify the feasibility for filling current CNT markets. While the size of current CNT markets would be small, relative to the size commensurate with H₂ production, identification of existing markets could spurn interest and provide critically required investment from DOE and private sources. We have identified commercial partners who see the potential value in the ReCaP's CNTs and are willing to invest their own resources into this endeavor. Just as important, this commercial partner brings a wealth of experience in CNT processing and can be a helpful partner in identifying and developing new, large volume markets that would make the economics for PNNL's CNTs and H₂ advantageous.

The scope proposed here will i) scale up CNT production using a fluidized-bed reactor (25 g scale) and generate at least 25 g of raw CNT product, ii) characterization of ReCaP CNT before and acid wash purification, prior to sending to industrial collaborators for application testing, and iii) techno-economic and market analysis of market relevance for processed CNTs relative to commercial competitors using \$/kg for blinded feedstock provided by industry partners.

2.0 Experimental

We demonstrated the performance of the ReCaP process in a fluidized-bed reactor operated at 550-650°C and 300 sccm of 100 to 10 vol% CH₄. The CH₄ conversion and H₂ production were monitored with an on-line GC. After reaction, the content of the reactor (i.e., solid co-products) was retrieved and weighed to determine the carbon yield and saved for surface area, density, thermogravimetric analysis, and Raman spectroscopy analysis. A fraction of the CNT co-products was acid washed to remove metals from catalysts. Samples of the materials after reaction and after acid wash were sent to industrial collaborators for property testing. We built a preliminary TEA model to compare the performance and costs against current direct wastewater discharge costs to identify key areas of optimization.

3.0 Results and Discussion

3.1 Effect of reaction conditions of catalyst performance

Table 1 summarized the performance of the proprietary ReCaP catalyst in the fluidized bed under different reaction conditions. The key catalyst performance such as the carbon yield (i.e., mass of carbon deposited per g of catalyst) increases by nearly two orders of magnitude from 5 to 500 g_C/g_{cat}. Changing reaction temperature from 550 to 650°C improve the single-pass conversion. Changing the flow rate from 150 to 450 sccm did not noticeably changed the conversion suggesting that the system was no operating under a kinetically relevant regime; hence, a combination of equilibrium limitations as well as heat and mass transfer limitations were controlling the system.

Future work will focus on optimizing the catalyst formulation to operate under different reaction regimes as well as modify the reactor design to improve heat and mass transfer across the fluidized catalyst bed.

Table 1. Summary of reaction conditions tested and effects on key performance parameters.

Run	Catalyst loading, g	Temperature, °C	Feed Flowrate, sccm	[CH ₄], vol%	WHSV, h ⁻¹	Carbon yield, g/g _{cat}	Carbon produced, g	Time on Stream, h
176	25	600	300	100	0.5	2.91	72.7	33
177	25	600	300	100	0.5	6.60	165	68
178	25	600	300	100	0.5	2.00	50.0	15
179	25	640	300	100	0.5	5.28	132	44
180	25	600	300	100	0.5	18.9	473	260
181	5	600	300	100	2.5	19.4	97.0	105
182	5	600	300	10	2.5	2.50	12.5	22
183	5	600	300	10	2.5	8.08	40.4	126

3.2 Effect of reaction on CNT properties

Figure 1 summarized the relationship of CNT properties as function of carbon yield. For all the properties evaluated in this work (e.g., surface area, CNT particle density, Raman ID/IG ratio), there was a linear dependency between the carbon yield and the different properties. For example, as the carbon yield increases, we expect the CNTs to grow in length and intertwine with adjacent CNTs; hence, increasing the density and surface area (Figure 1a). Surprisingly, the Raman derived ID/IG ration also increased with carbon yield, suggesting the at the morphology of the CNTs (e.g., aspect ratio of length vs diameter, number of walls) also changed. The produced CNTs were sent to the industrial collaborators for evaluation in their respective processes.

Future work will focus on characterizing the properties of the different produced CNTs with TEM and SEM to correlate their morphology to the carbon yield. Additionally, we will evaluate the utilization of the produced CNTs as additives in the manufacturing of high-performance materials such as cement and polymer composites.

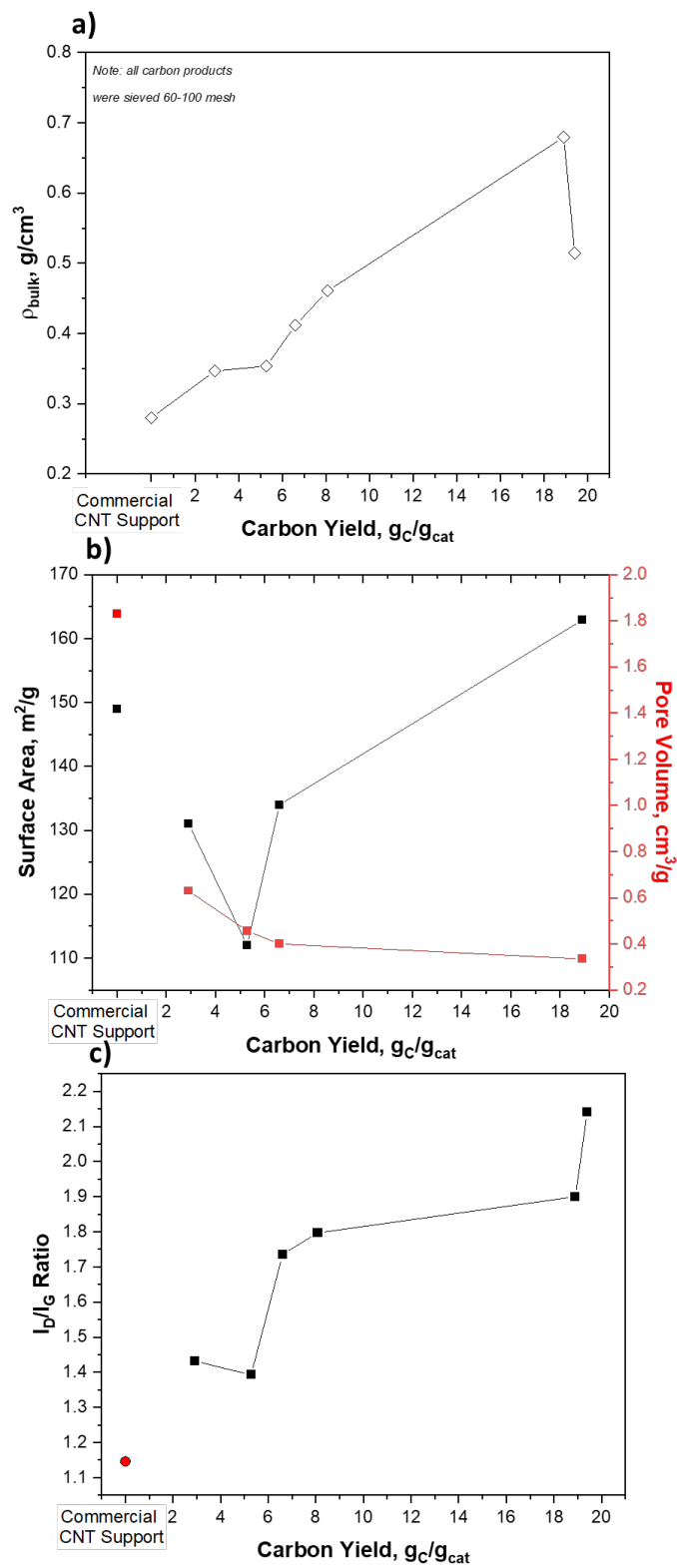


Figure 1. Properties of CNT co-product as a function of carbon yield.

3.3 Techno-economic analysis

Figure 2 summarizes the relationship between the minimum H₂ selling price (MH₂SP) and the solid CNT co-product credit for a H₂ production facility of 100,000 MT/y facility. The MH₂SP without any credit for CNT is \$5.57/kg; however, increasing the CNT credit to \$1.17/kg would decrease the MH₂SP to \$2.0/kg. The DOE Hydrogen Earthshot goal of \$1/kg can be met by increasing the CNT co-product credit to \$1.7/kg. The inclusion of 45Q Carbon Tax and optimization of the TCD system would result in a lower MH₂SP.

Future work will perform a sensitivity analysis on the MH₂SP using the key process parameters optimized in this study to identify key areas of optimization.

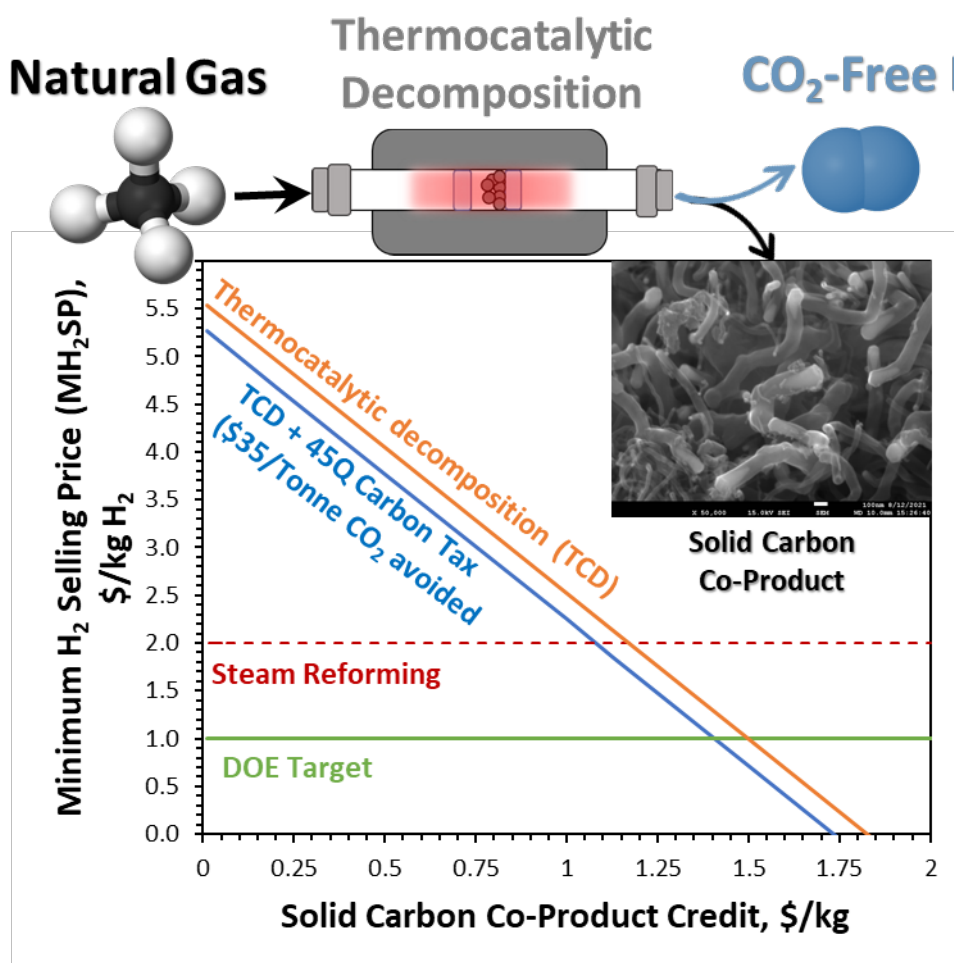


Figure 2. Relationship between the minimum H₂ selling price and solid carbon co-product credit.

4.0 References

1. Xu, M.; Lopez-Ruiz, J. A.; Riedel, N. W.; Weber, R. S.; Bowden, M. E.; Kovarik, L.; C., J.; Hu, J.; Dagle, R. A., Promotional role of Ni-Cu alloy in catalytic performance and carbon properties for CO₂-free hydrogen production from methane decomposition. *Catalysis Science & Technology* 2023, (13), 3231 - 3244.2.
2. Jiang, J.; Lopez-Ruiz, J. A.; Bian, Y.; Sun, D.; Yan, Y.; Chen, X.; Zhu, J.; May, H. D.; Ren, Z. J., Scale-up and techno-economic analysis of microbial electrolysis cells for hydrogen production from wastewater. *Water Res.* 2023, 241, 120139.3.
3. Jiang, C.; Wang, I. W.; Bai, X.; Balyan, S.; Robinson, B.; Hu, J.; Li, W.; Deibel, A.; Liu, X.; Li, F.; Neal, L. M.; Dou, J.; Jiang, Y.; Dagle, R.; Lopez-Ruiz, J. A.; Skoptsov, G., Methane Catalytic Pyrolysis by Microwave and Thermal Heating over Carbon Nanotube-Supported Catalysts: Productivity, Kinetics, and Energy Efficiency. *Industrial & Engineering Chemistry Research* 2022, 61 (15), 5080-5092.4.
4. Dagle, R. A.; Lopez-Ruiz, J. A.; Xu, M.; Riedel, N. W.; Weber, R. S.; Hu, J.; Jiang, C. PRODUCTION OF CO₂-FREE HYDROGEN AND CARBON NANOMATERIALS BY METHANE DECOMPOSITION: SELF-SUSTAINED PRODUCTION WITHOUT USING EXTERNALLY ADDED CATALYST. 2022.5.
5. Xu, M.; Lopez-Ruiz, J. A.; Kovarik, L.; Bowden, M. E.; Davidson, S. D.; Weber, R. S.; Wang, I. W.; Hu, J.; Dagle, R. A., Structure sensitivity and its effect on methane turnover and carbon co-product selectivity in thermocatalytic decomposition of methane over supported Ni catalysts. *Appl. Catal. A-Gen.* 2021, 611, 117967.

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