North Dakota Renewable Energy Program

Final Report

R-050-066

PRODUCTION OF HYDROGEN AND VALUABLE CARBONS FROM METHANE-SOURCES

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PROJECT SUMMARY

Purpose: The project aimed to develop and optimize a process for producing renewable hydrogen and high-value carbon through methane decomposition using a thermocatalytic system. The goal was to achieve a levelized cost of hydrogen of $2.00/kg by integrating the produced carbon into practical applications, such as batteries. Additionally, the project explored the feasibility of utilizing renewable natural gas for hydrogen production, recognizing hydrogen's crucial role as a precursor in ammonia manufacturing and its significance within North Dakota's agricultural sector.

Work Accomplished: The University of North Dakota and project partner Envergex LLC, employed its thermocatalytic system to decompose methane into a type of nano-carbon, akin to carbon nanofibers and carbon nanotubes available commercially. Various catalysts were tested, with a nickel-based catalyst supported on alumina and silica achieving the highest methane conversion (up to 70%) and the longest catalytic activity. Other tested catalysts, including iron-based and carbon-based materials, did not exhibit comparable reactivity. The produced carbon was processed for use in coin cell test batteries, replacing up to one-third of the carbon black in lithium iron phosphate coin cell cathodes. Additionally, operating schemes for hydrogen production were developed, utilizing historic and current electricity pricing data to optimize system size and operation through the selective use of electricity and/or natural gas for heating. Alternative processing schemes combining decomposition and electrolysis technologies were also explored.

Results: The coin cells containing the produced carbon achieved over 50% higher specific capacity densities compared to baseline cells, containing only commercial carbon black, after 100 cycles of charging and discharging. The tests confirmed the carbon's effectiveness as a conductivity enhancer.

The positive results supported the economic viability of the process. Costing models were developed to evaluate how various heating methods and the integration of small electrolyzers into a conventional decomposition process could help mitigate fluctuations in gas and power prices. Specifically, using renewable natural gas as a feedstock and pure electricity for heating the decomposition process, the approach pathway achieved a levelized cost of hydrogen of $2.00/kg, provided the carbon was sold at approximately $1.60/kg, comparable to commercially available carbon black. The process was competitive with green and blue hydrogen and remained cost-effective compared to gray hydrogen ($1.00/kg hydrogen) when the carbon selling price was equal or greater than $1.60/kg. Given that commercial carbon nanotubes can exceed $500/kg, further research into this technology is warranted to explore ways to monetize the carbon produced.

Potential Applications: The produced carbon has potential uses as a conductivity enhancer in lithium iron phosphate batteries, showing a specific capacity maintaining effect. The developed hydrogen production processes and simulation tools offer a cost-effective method for developers to generate renewable hydrogen, which is beneficial for industries dependent on hydrogen, such as ammonia production. For North Dakota, this project supports the viability of renewable natural gas options, pathing the way for leveraging local agricultural waste and livestock to meet hydrogen demands sustainably. Additional work is required to precisely characterize the carbon formed and assess its long-term performance in battery applications.

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1. Objectives of the Project

The main objective of this project was to reduce the cost of renewable hydrogen (H_2) to <\$2.00 per kilogram (kg) by decomposing biomethane via a catalytic decomposition process. The catalytic decomposition of methane (CDM) reaction is endothermic, requiring about 38 kJ/mol-H_2 to break up CH_4, several-fold less energy than water electrolysis (~280 kJ/mol-H_2). Whereas steam methane reforming generates CO_2 gas, requiring pressurization and geologically sequestering, CDM generates solid carbon eliminating the need for costly and complex CO_2 capture and sequestering. The key to this technology is integrating electrical and combustion heating to overcome the challenges associated with the intermittency of renewable power sources like wind or solar. If in the form of carbon nanotubes (CNT), CDM-derived carbon also has potential uses in lithium-ion batteries (LIBs). The synthesis parameters influence the carbon's type, quality, and value. Depending on the type, CNT costs can range from \$500/kg to \$2-million/kg.[1,2]

A secondary aspect that needed to be addressed was how to provide H_2 producers the opportunity to seamlessly integrate intermittent renewable power technologies into their manufacturing systems and decrease the cost of renewable or green H_2 compared to other green H_2 production technologies. Green H_2 is currently much more expensive than gray (\$2.50/kg - \$4.50/kg for green vs. \$1.25/kg - \$2.00/kg for gray)[3]. Gray H_2 is derived from fossil fuels. This project aimed to decrease the cost difference between green and gray H_2 by improving the energy utilization of the production process and providing valuable CNTs to battery manufacturers. For every 1.00 kg CH_4 converted, 0.75 kg of C and 0.25 kg of H_2 can theoretically form. Valuable carbon can help reduce the cost of H_2 even further and position North Dakota, with vast biomass-based resources, as a leading renewable resources provider in the U.S.A.

In order to meet the project objectives, the following tasks were completed (note the tasks start at 6 as they were incorporated into the original Department of Energy project, DE-FE0032061, which contained 5 tasks):

Task 6 – Evaluation and Characterization of Carbon Products:

UND used a laboratory-scale thermocatalytic CH_4 conversion system to produce and collect carbon as part of the DE-FE0032061 project. The carbons that were formed during this process were assessed for use in LIB electrodes. UND firstly collected and then characterize the carbons to see if they exhibit the characteristics of high-quality CNTs. The focus of this task was to understand how the operating conditions of the cleaning system affected the size and purity of the removed carbon species and whether the conditions that maximize H_2 production also corresponded with high-quality CNT synthesis. Due to limitations in the size of the equipment, insufficient amounts of carbon were removed from the catalyst, despite the recipient validating the proposed technology, with scanning electron microscopy images corroborating the removal of deposited carbon from the surface of the catalyst. However, the recipient was able to generate gram quantities of carbon and separate the carbon ex-situ of the decomposition reactor to obtain >90% pure carbon and >95% pure carbon when subjected to a washing step. This washing step would

[1] L. Bromberg, D. R. Cohn, A. Rabinovich, C. O'Brien, and S. Hochgreb, *Energy and Fuels*, vol. 12, no. 1, pp. 11–18, 1998.

[2] L. Chen, Z. Qi, S. Zhang, J. Su, and G. A. Somorjai, *Catalysts*, vol. 10, no. 8, 2020.

[3] R. Vander Wal and M. Makiesse Nkiawete, *C — J. Carbon Res.*, vol. 6, no. 2, p. 23, 2020.

likely not be required if the in-situ carbon removal technique is scaled up.

Following the retrieval and characterization of the carbon, the same material was used to manufacture CR2032 coin-type cell (for lab-scale samples). Current densities and specific capacities were calculated (with 170 mAh/g being the theoretical specific capacity of lithium iron phosphate) based on the mass of the target compound of the electrode. Cycle life was evaluated by using a three-electrode system (ECC-REF, EL-Cell GmbH, Germany) for cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests. In total, three different coin cells were produced, with the first group replacing all of the carbon black with the produced carbon, the second group replacing just over 10% of the carbon black, and the third group replacing just over 25% of the carbon black.

The test groups, along with a repeat and control group (100% carbon black, 0% produced carbon) are given in Table 1. N-methyl-2-pyrrolidone (NMP) was used as an organic solvent to help manufacture the coin cells. Polyvinylidene fluoride (PVDF) was used as a binder, and a commercially procured carbon black (XC-72) was used as the main carbonaceous component in the coin cells. The LFP active component made up 85 % by weight of each group.

Table 1: Test groups with different percentages of carbon incorporation into the coin cells.

Element	Control group	Test group 1 (7.5% carbon)	Test group 2 (1% carbon)	Test group 2 (1% carbon) Duplicate	Test group 3 (2.5% carbon)
Organic solvents	NMP (2g)	NMP (2g)	NMP (2g)	NMP (2g)	NMP (2g)
Binders	PVDF (7.5%)	PVDF (7.5%)	PVDF (7.5%)	PVDF (7.5%)	PVDF (7.5%)
Conductive material	XC-72 (7.5%)	Project Carbon (7.5%)	XC-72 (6.5%) + Project Carbon (1%)	XC-72 (6.5%) + Project Carbon (1%)	XC-72 (5%) + Project Carbon (2.5%)
Active material	LFP (85%)	LFP (85%)	LFP (85%)	LFP (85%)	LFP (85%)

Eight coin cells were assembled for each test group, with three coin cells undergoing 20 cycles of low-rate charging (0.2C) to evaluate their performance under moderate charging and discharging conditions. Additionally, 3 coin cells were tested with high-rate charging (1C) for 100 cycles to assess their durability and performance under more demanding conditions. Two coin cells served as backups for each group. This testing was conducted to assess the carbon's effectiveness across different charging rates and ensure its suitability for practical applications.

The results from Task 6 is discussed under section "2. Results and Discussion".

Task 7 – Process Model of Greener H₂ Production System: UND and Envergex developed a software toolkit that uses variable grid prices for electricity as input, along with detailed capital and operating costs for electrically-based heating systems, combustion-based heating systems, combinations thereof, and a hybrid model combining an electrolyzer with a conventional methane decomposition process using a combustion-based heating system. UND and Envergex evaluated

the net present value of investments into the proposed H_2 manufacturing processes across different scenarios. The scenarios were assessed using spreadsheets and Aspen Plus. The information was used in an iterative fashion to optimize the designs.

Different H_2 production methods, using renewable natural gas as the methane source for decomposition, were used to better understand the path to commercialization. The analysis aimed to achieve a target production rate of 1 tonne per hour (tph) H_2 while evaluating various modes of operation as follows:

i.   Methane decomposition using H_2-Air combustion (100C) for heat provision (Figure 1):

The pyrolysis process utilized hydrogen-air combustion, with a basic configuration comprising a reactor for decomposition, a baghouse to capture and remove carbon, and pressure swing adsorption (PSA) to purify the H_2. Key aspects of this setup included the combustion of a portion of the produced hydrogen, specifically 0.2 tph, while generating a total of 1.2 tph of hydrogen. This approach ensured a CO_2-free process, optimizing both hydrogen production and environmental sustainability.
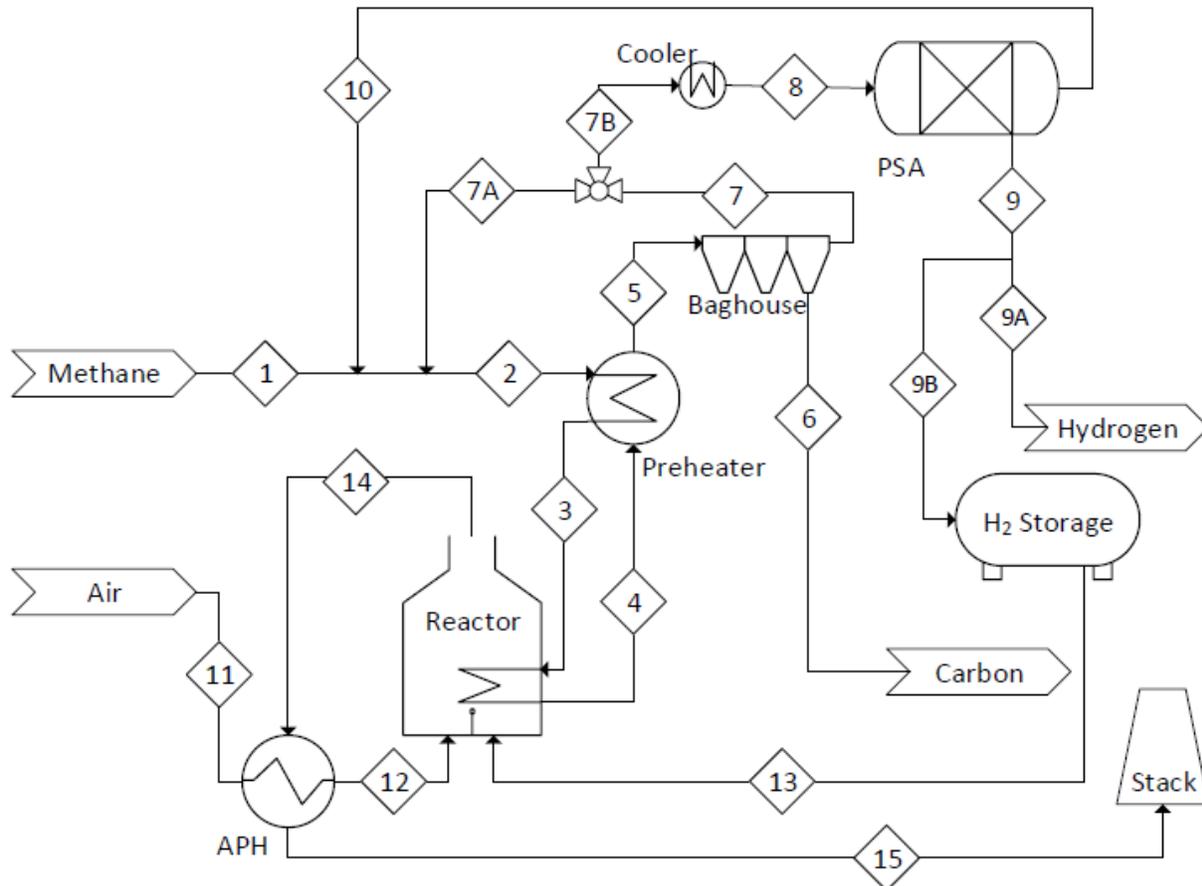

Figure 1: Pyrolysis 100C-mode hydrogen plant.

ii.   Methane decomposition using pure electric heating (100E), (Figure 2):

The pyrolysis process with pure electric heating (100E) utilized a basic configuration similar to the 100C case, including a reactor, a baghouse, and PSA. This setup employed 100% electric heating and was designed to produce 1 tph of H_2, with the recycling of unconverted feedstock.
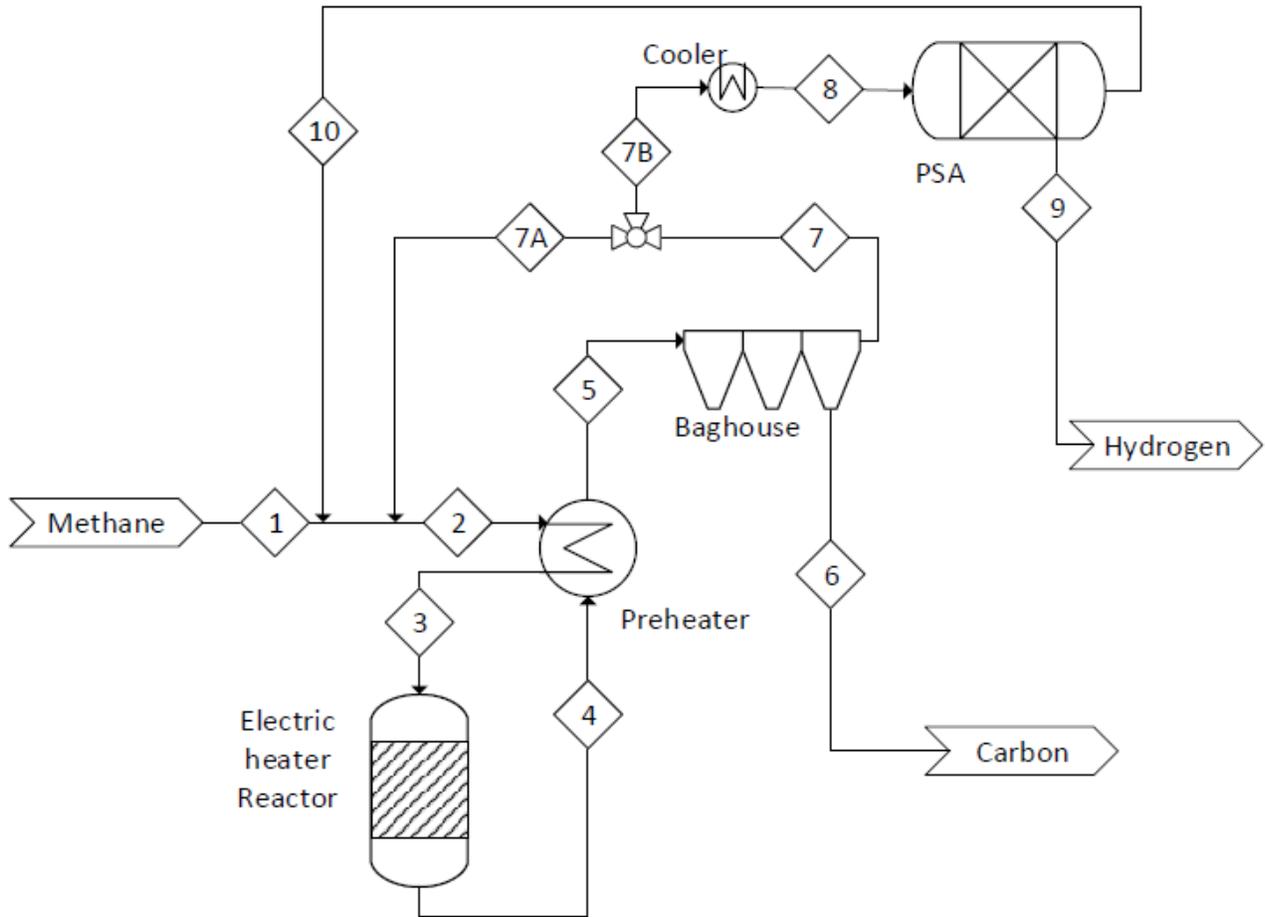

Figure 2: Pyrolysis 100E-mode hydrogen plant.

iii.   Methane decomposition via decomposition and electrolysis, with the electrolyzer producing H_2 as a product and supplying O_2 for combustion with unconverted feedstock (Elec-Pyro), (Figure 3):

The pyrolysis-electrolysis process with feedstock-O_2 combustion (Elec-Pyro) utilized a basic configuration similar to the previous setups, including a reactor, a baghouse, and PSA. Unlike the other cases, this setup incorporated electrolyzers for hydrogen production. Specifically, the process produced hydrogen through electrolysis for 20% of the output and CDM for the remaining 80%, generating 1 tph of H_2.

Oxygen was used for the combustion of unconverted feedstock. Although the process produced CO_2, it included CO_2 capture and recycling for temperature control, ensuring no direct CO_2 emissions.
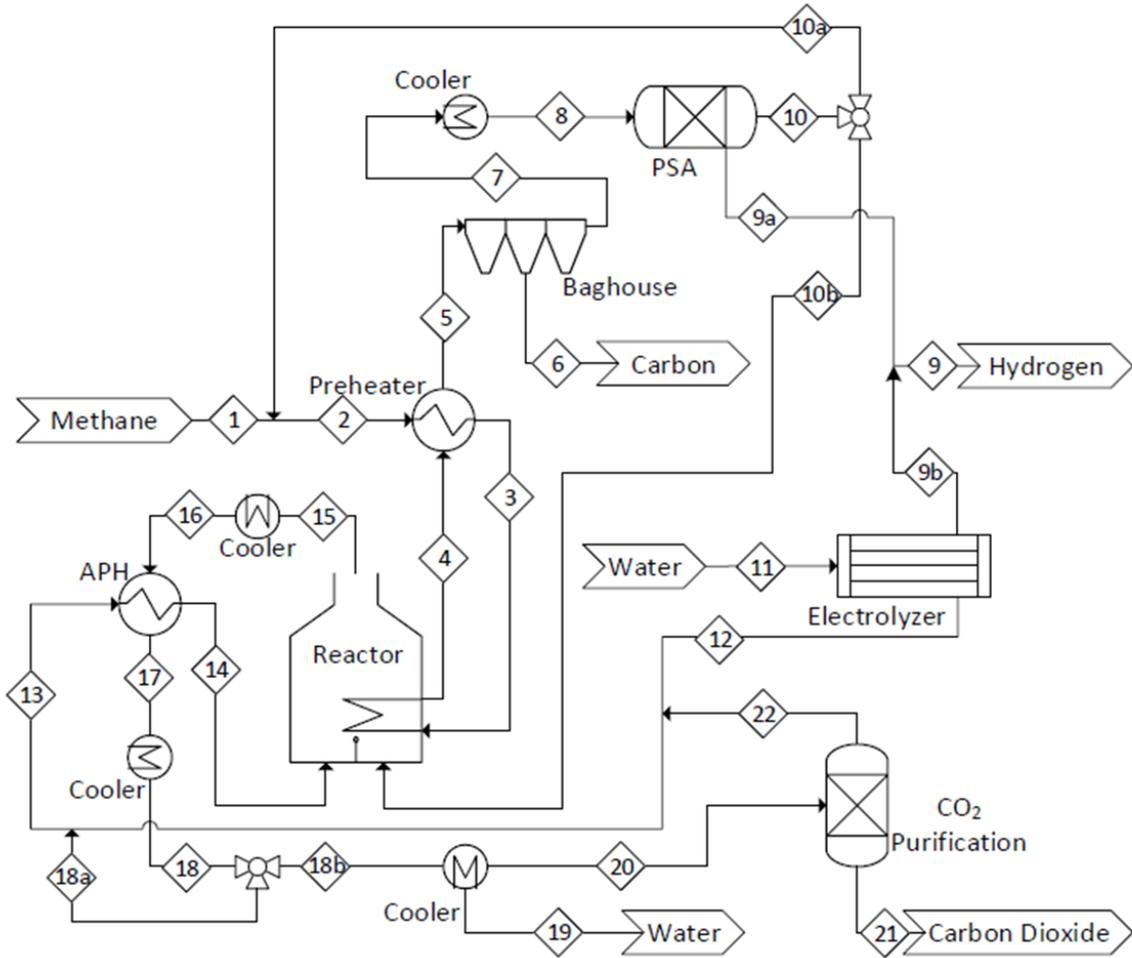

Figure 3: Electrolysis-Pyrolysis hydrogen plant.

iv.   Methane decomposition using a hybrid approach combining combustion and electric heating, with configurations of 30% electric heating (30E), 50% electric heating (50E), and 70% electric heating (70E), with the remainder provided by combustion heating.

These cases were assessed by assuming there would be no additional capital expenses associated with using a combined electric and combustion heating approach. Catalytic systems can be heated in numerous ways and this was deemed a reasonable assumption to assess how different configurations would affect the LCOH.

v. Water electrolysis for H$_2$ production used as a comparative case (Electrolysis)

This case was used for comparative purposes and only used an electrolyzer for producing 1 tph H$_2$. This case would be only dependent on the cost of electricity and represents green H2 at conditions relevant to North Dakota with its electricity pricing.

To conclude this section, key aspects of each configuration were assessed, including production rates, combustion methods, and CO$_2$ emissions. Sensitivity analyses addressed factors such as capital expenditure (CAPEX), gas and power pricing, and catalyst costs.

The results from Task 7 is discussed under section "2. Results and Discussion".

2. Results and Discussion

Task 6: Evaluation and Characterization of Carbon Products

Characterization of carbon products: Iron, silica aerogel, carbon, and bimetallic catalysts such as iron/copper and nickel/copper were tested for their methane cracking ability. The nickel catalyst supported on a porous silica and alumina structure provided the longest (over 2000 minutes) reactivity. Due to the high methane conversion capability (over 70% conversion), this catalyst was chosen as the target material for the carbon generation analyses. The produced carbon using a nickel-based catalyst is shown in Figure 4.
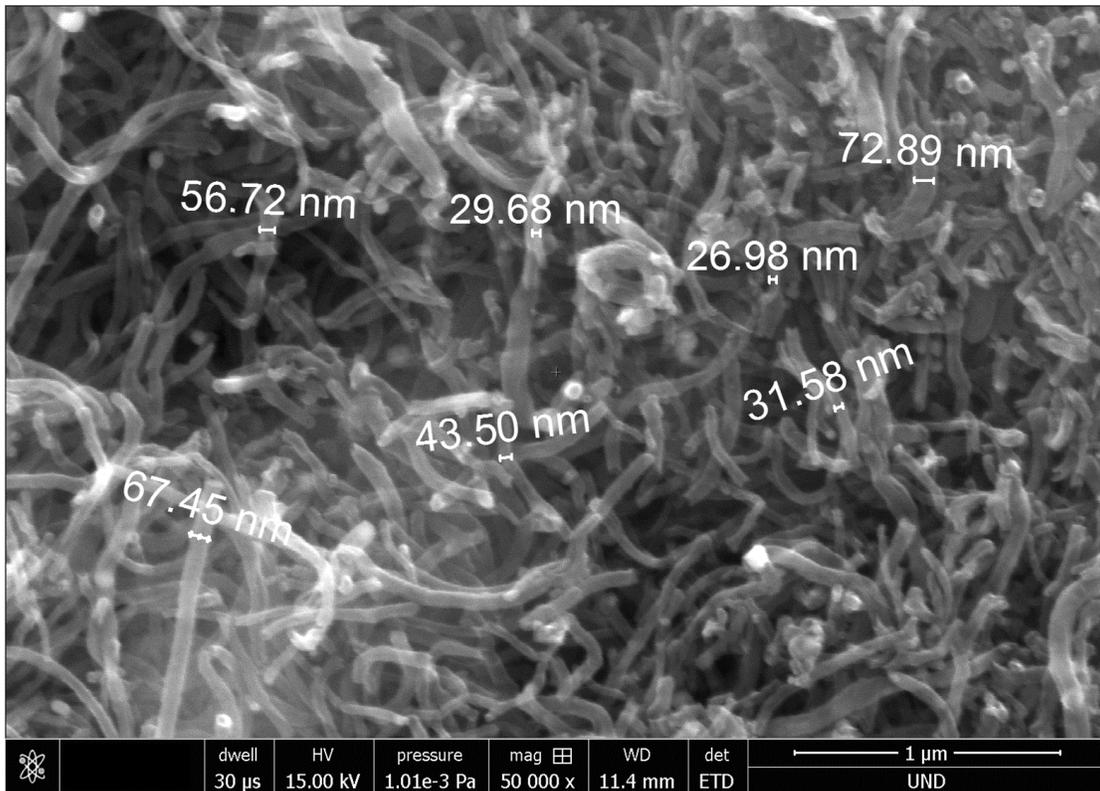

Figure 4: Nano-carbon compounds produced via the catalytic decomposition of methane.

This material was similar in structure to products sold commercially as 99% high purity multi-walled carbon nanotubes and nanofibers of 10-200 nm outer diameter shown in Figure 5. Based on these observations, the carbon was tested for purity using a total carbon analyzer. The results indicated a carbon content of 91 wt.%.

These results were confirmed via a thermogravimetric analysis of the carbon whereby the material was heated in an inert environment up to 850˚C, with only 5% weight loss, and following this the sample was combusted in 20% oxygen with 5% ash remaining. Therefore, the carbon was at least 90% pure. After washing, a 95% carbon purity was obtained.
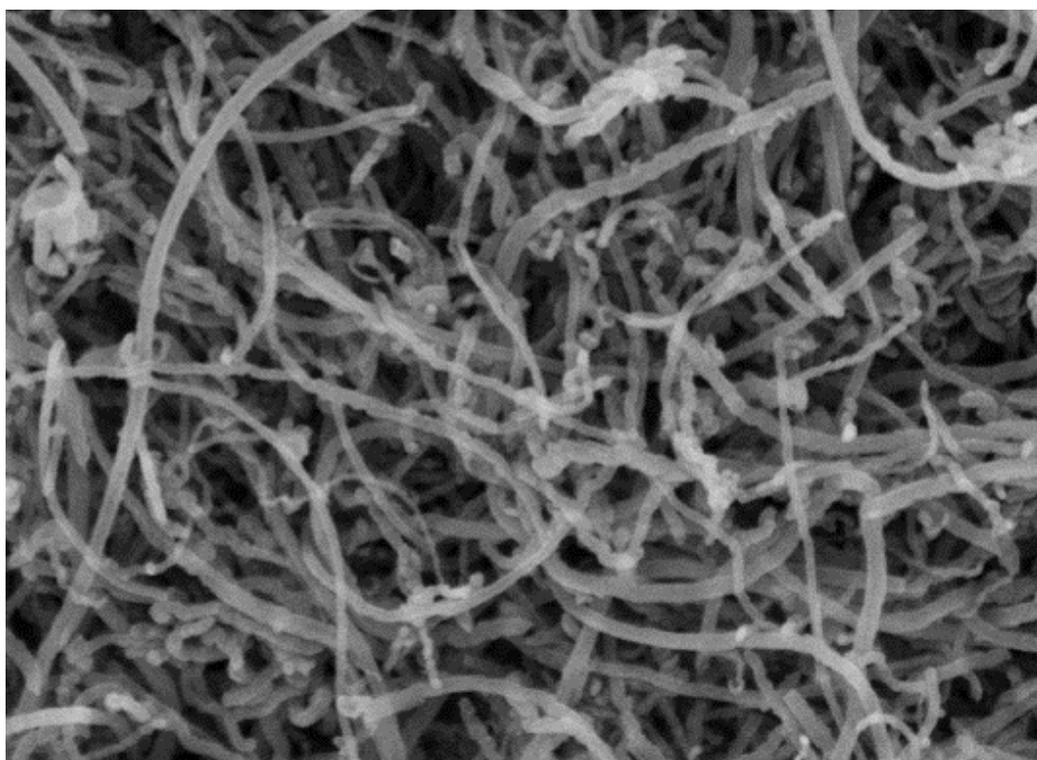

Figure 5: MSE PRO 10g Battery Grade 99% High Purity Multi Walled Carbon Nanotubes and 99.9% Carbon Nanofibers.[4]

For comparison, the catalyst surface after regeneration (Figure 6) showed traces of the tubes remaining, and it is therefore expected that a pure carbon product can be attained if a large enough catalyst regeneration system is configured.

In addition to the SEM results, a final transmission electron microscopy (TEM) analysis was conducted to assess whether the nano-compounds were carbon nanotubes. Figure 7 shows the TEM result, with a catalyst particle indicated by the dark region surrounded by the added yellow line.
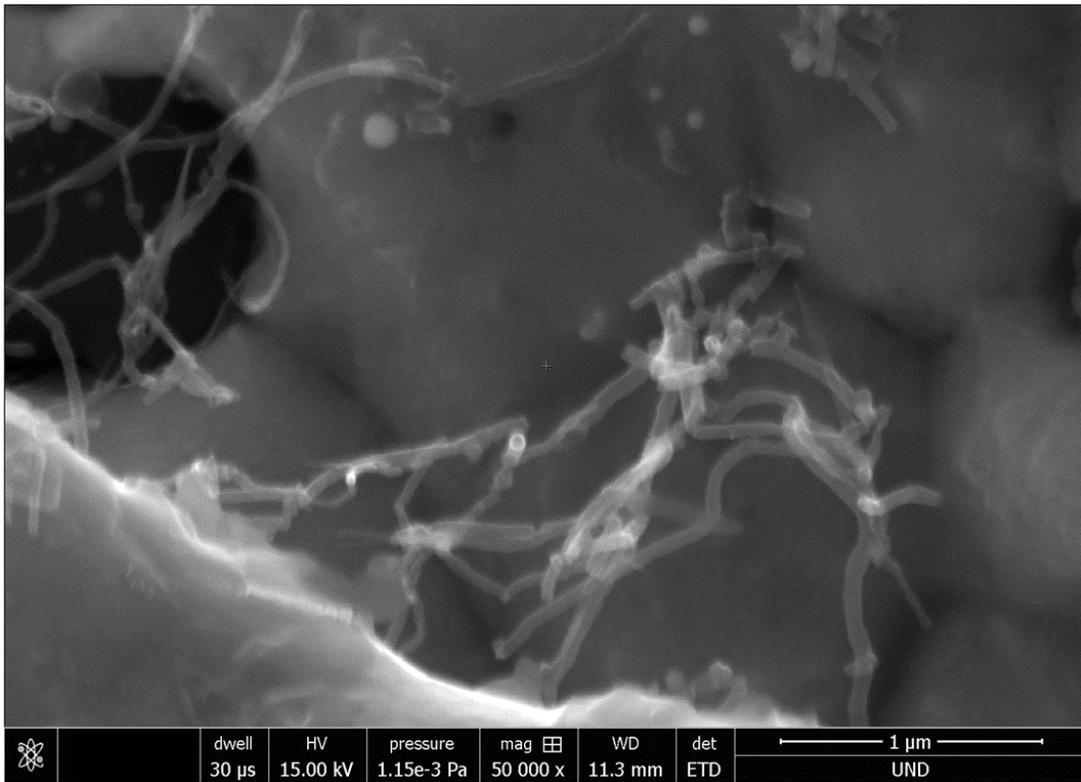
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[4] https://www.msesupplies.com/

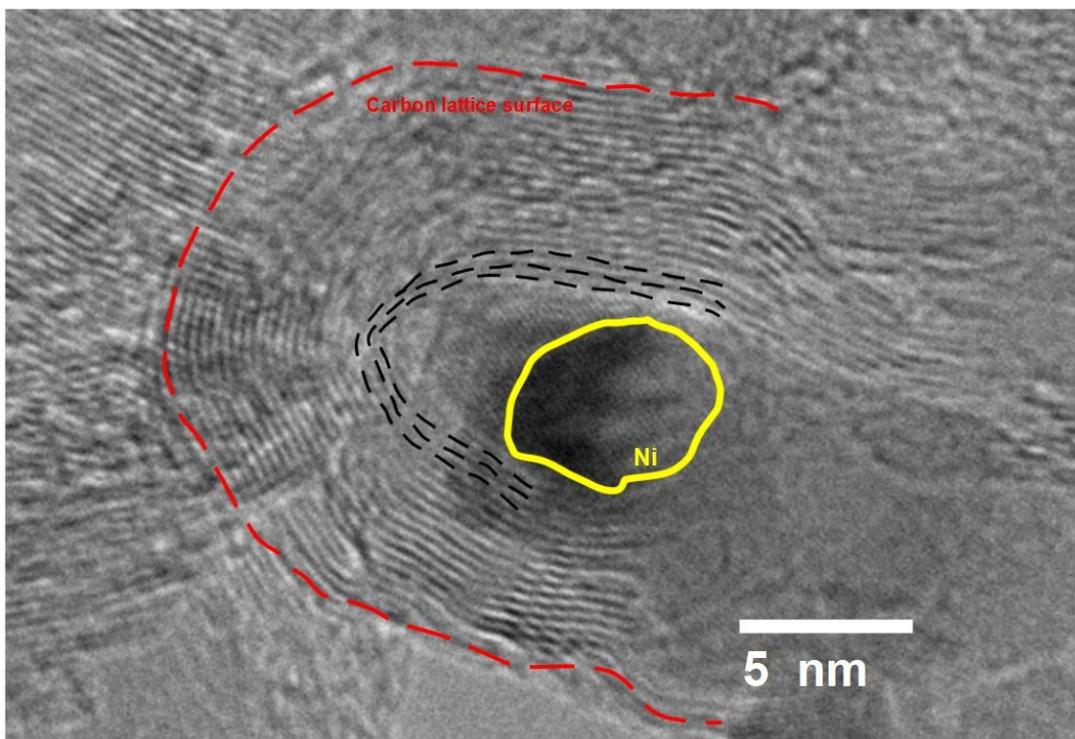**Figure 6:** Catalyst surface after carbon removal.

Figure 7: High resolution transmission electron microscope (TEM) image of the carbon product.

The carbon lattice structure was visible, but from the image, the material did not exhibit the tell-tale hollow structure of typical nanotubes as depicted in literature (Figure 8). The washing and subsequent size reduction could have likely damaged the carbon structures.

Another possibility is that as the CDM process continued, initial carbon nanotubes could have catalyzed the further decomposition of methane, leading to other forms of carbon than expected. These are future research questions that would need to be addressed in order to definitively characterize the type of carbon produced.

For the purposes of this study, the bulk prepared carbon sample was used for the battery testing.
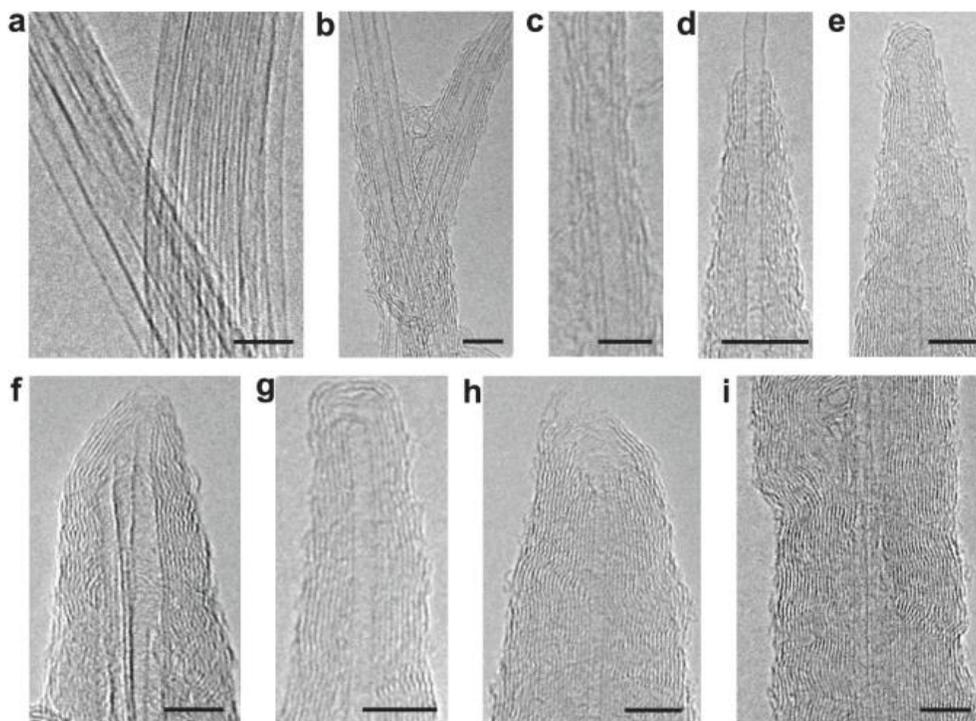

Figure 8: High-resolution TEM images of graphene layers grown on SWCNTs [taken from Li et al. (2013)][5]

Evaluation of carbon products: The recipient focused on evaluating battery performance through C-rate testing, where C-rate represents the current for both charge and discharge processes. In battery testing, the C-rate is a measure of the rate at which a battery is charged or discharged relative to its capacity. The C-rate is expressed as a multiple of the battery's capacity, denoted as "C". For example, a C-rate of 1 indicates the ability to fully charge the battery in 1 hour, while 0.2C corresponds to a 5-hour charging and discharging cycle. The choice between 0.2C and 1.0C is important, as lower C-rates (e.g., 0.2C) are often used for testing, known as low-capacity testing, to assess cycle life, while higher currents (1.0C) simulate high-demand scenarios.

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[5] Li, K., Eres, G., Howe, J., Chuang, Y.J., Li, X., Gu, Z., Zhang, L., Xie, S. and Pan, Z., 2013. Self-assembly of graphene on carbon nanotube surfaces. *Scientific reports*, *3*(1), p.2353.

The results from the 0.2C tests are shown in Figure 9. The coin cell with 7.5% project carbon performed the worst (Test group 1) compared to the other coin cell groups. The control group as well as groups 2 and 3 performed very similar. The result showed that too much commercial carbon replacement lowered the battery's specific capacity density by about 30%.
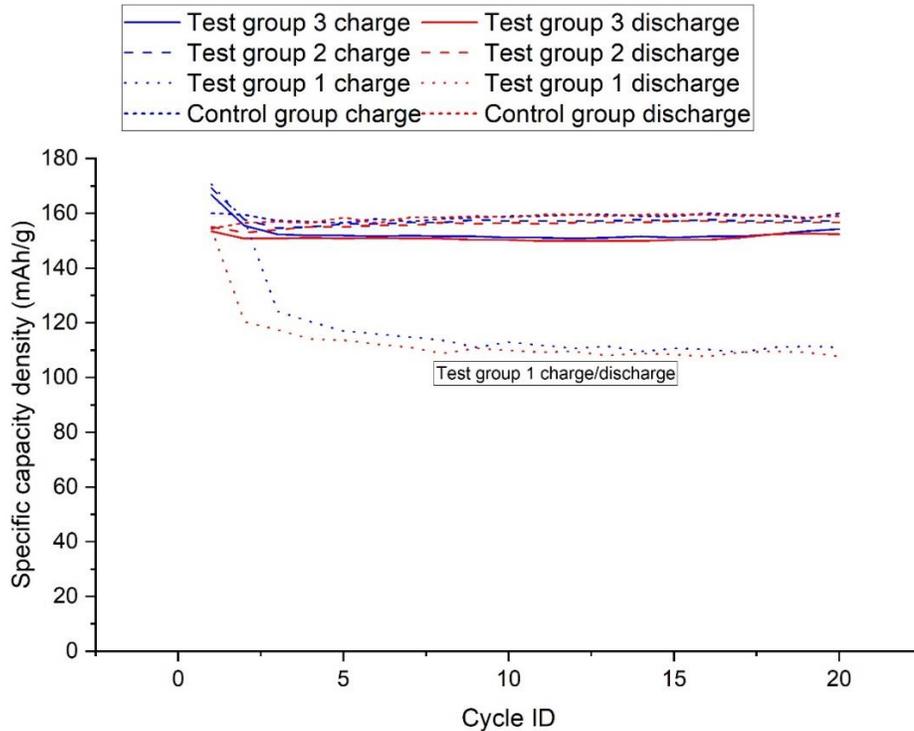

Figure 9: Low C rate (0.2C) life cycle comparison. Test group 1 - 7.5% project carbon; Test group 2 – 1% project carbon; Test group 3 – 1% project carbon; Control group – 7.5% commercial carbon.

The results from the 1.0C tests are shown in Figure 10. In comparing the high C-rate life cycles, the control group coin cells charged at 1.0 C for 100 cycles exhibited typical expected capacity loss. Notably, cells with a high project carbon content levels of 7.5% (Test group 1) demonstrated poorer performance, despite showing better stability compared to the control group. In contrast, cells with lower project carbon levels, specifically 1.0% to 2.5% (Test group 2 and 3, respectively), outperformed the control group by over 50% based on the coin cell's specific capacity density at cycle 100, indicating superior performance.

These trend highlight the role of conductive agents in enhancing performance during high C-rate charging and discharging activities, as their effectiveness is typically more pronounced under such conditions. Figure 11, for example, shows the electrochemical performance of LFP-impregnated carbon fiber electrodes with different additives. Yücel *et al.* (2024)[6] indicated that the electrochemical cycling performances align closely with the electrical conductivity of the electrodes; therefore, it is well-established that conductive additives play a significant role in enhancing the high C- rate performance of batteries.[6] Ultimately, the charging and discharging

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[6] Yücel *et al..*, 2024. Enhancing structural battery performance: Investigating the role of conductive carbon additives in LiFePO4-Impregnated carbon fiber electrodes. *Composites Science and Technology*, *251*, p.110571.

process of lithium batteries requires the transfer of lithium ions and electrons, which is manifested in the external macroscopic form of current. Conductive agents such as graphene, for example, can be used as small particles of molecular materials surrounding the active material of the electrode to create more contacts and thus facilitate electron transfer.
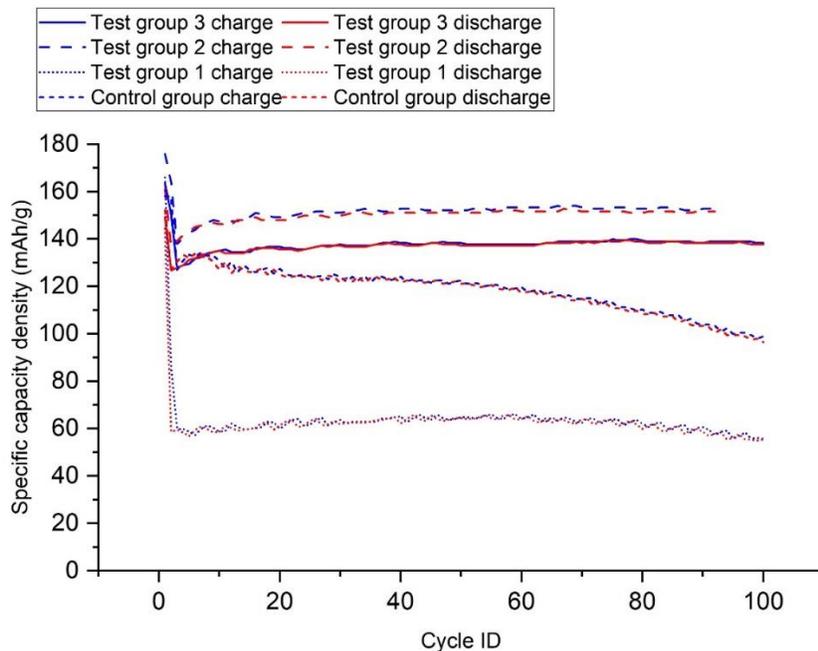

Figure 10: High C rate (1C) life cycle comparison. Test group 1 - 7.5% project carbon; Test group 2 – 1% project carbon; Test group 3 – 1% project carbon; Control group – 7.5% commercial carbon.
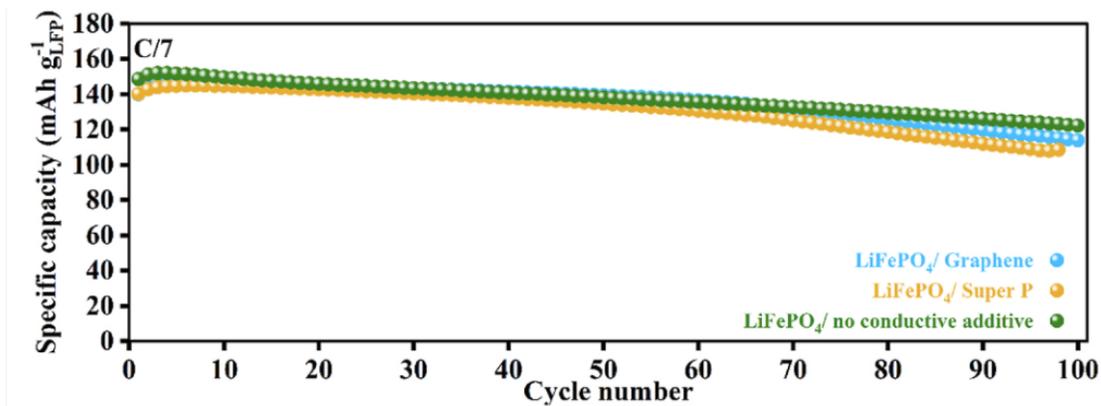

Figure 11: Electrochemical performance of LFP-impregnated carbon fiber electrodes with different additives (taken from Yücel et al., 2024).[6]

In conclusion, the initial tests proved useful in gauging the carbon product's marketability as a component in LFP batteries. However, additional characterization and coin cell testing is required to definitively prove the benefits of the produced carbon and whether it causes unobserved and deleterious secondary effects to the battery performance.

Task 7: Process Model of Greener H₂ Production System

Methane pyrolysis process modeling and optimization approach: Based on the simulation results, as well as the carbon characterization results from Task 6, a LCOH comparison was compiled assuming the produced carbon can be marketed as a carbon black supplement for improved battery performance at the same cost as commercial carbon black products (between $1-2/kg).

Figure 12 shows the LCOH of the pyrolysis-electrolysis, the fully electrically heated decomposition process, the fully combustion-heated decomposition process, and electrolysis-only routes. For this, the cost of renewable natural gas was taken to be $18/MMBTU. At a carbon product selling price of approximately $1.60/kg, an LCOH of $2.00/kg can be obtained using either a fully electrically heated or a pyrolysis-electrolysis hybrid system. The results show that using a fully combustion heating approach is also viable, however, the pyrolysis-electrolysis route provides better buffering capacity to potential fluctuations in electricity and gas costs.
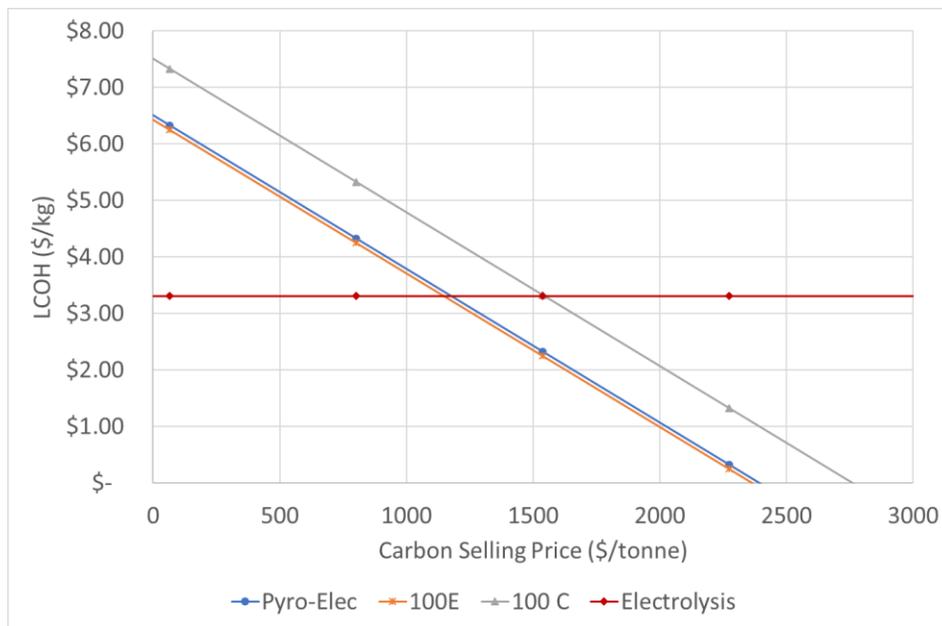

Figure 12: LCOH at different carbon selling prices.

To assess what combinations of electric heating and combustion heating would be feasible, a sensitivity analysis for changing power prices was conducted as shown in Figure 13. For this, the CAPEX for adding mixed-mode components to a plant was ignored. For this scenario, the cost of renewable natural gas was again assumed to be $18/MMBTU and the selling price for the carbon product was assumed to be $1.60/kg. The results show that the 100E (wholly electrically heated process) methane decomposition process always exhibited the lowest LCOH. These scenarios can vary and that is why the developed toolset is useful. It allows a particular user to input data from their specific region into the model and determine what would be a feasible process and configuration to use. Ultimately, the process for greener H₂ production can be cost competitive compared to green and blue H₂ if the carbon product can be sold when using renewable natural gas as feedstock. Without this, the process would not be able to compete with the other technologies.
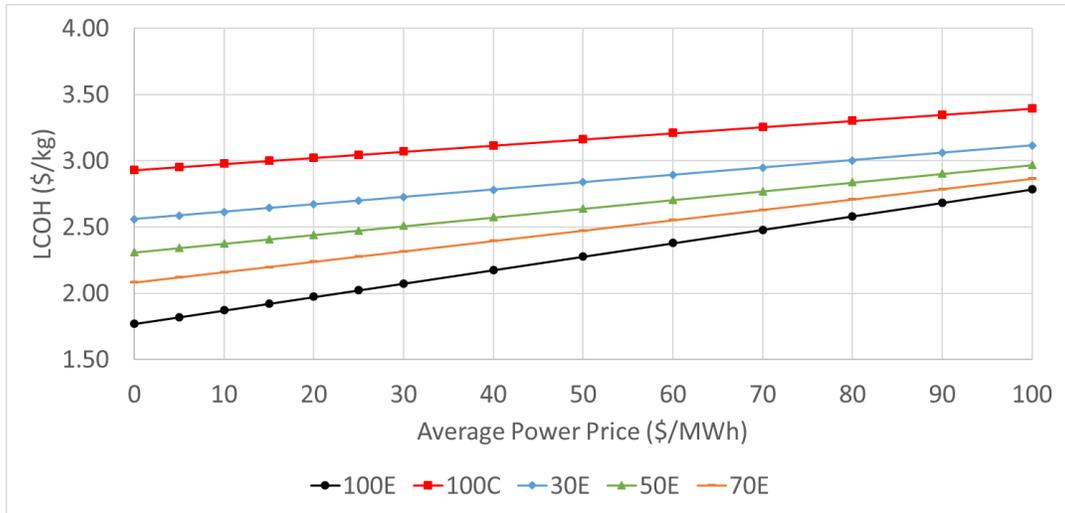
Figure 13: LCOH of pyrolysis plant designs using variations of electric and combustion heating – Assumed 0% CAPEX added for mixed mode plants.

Furthermore, within a setting where natural gas is available as a feedstock, the proposed methane decomposition process with a hybrid electrolysis-pyrolysis approach can yield LCOH values comparable to gray H_2 as shown in Figure 14. The vertical error bars indicate the results from the sensitivity analyses, and the horizontal lines indicate the minimum and maximum LCOH for gray H_2

In this case, the carbon product is assumed to sell at a value of $0.06/kg to cover the catalyst replacement cost. Any slightly higher carbon selling cost would be able to justify a carbon free (with near complete CO_2 capture and sequestration) hydrogen of green quality.
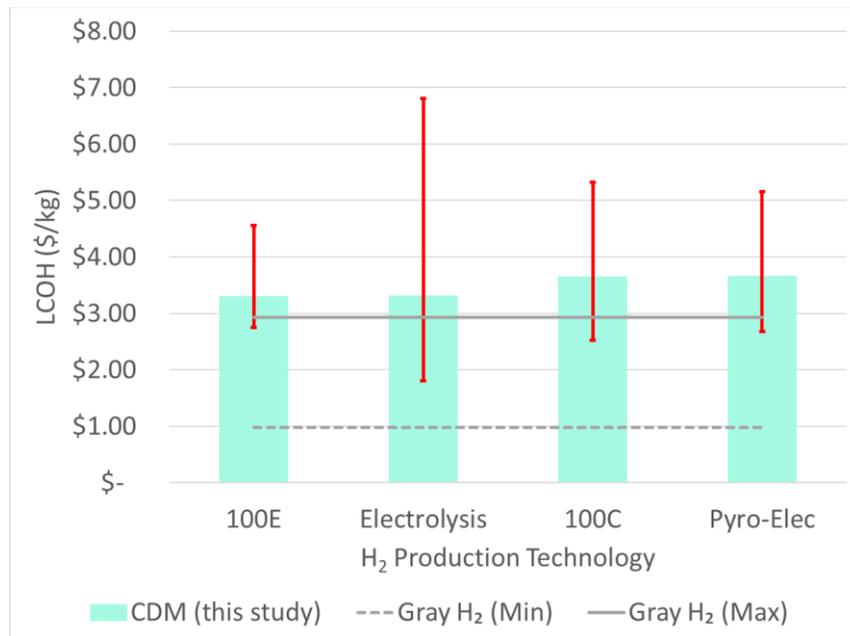

Figure 14: LCOH – Turquoise (referring to the catalytic decomposition of methane route) vs. gray H_2.

3. Conclusions and future prospects

The recipient addressed the main research questions regarding whether the methane decomposition process can produce a viable carbon product and achieve levelized cost of hydrogen (LCOH) values comparable to or lower than those of competing blue and green hydrogen technologies. The developed software tools utilize historical and current data to help the user make decisions on what degree of hybridization, if any, will be required for a specific operating region.

Although natural gas pyrolysis, utilizing a fossil raw material, does not represent a long-term sustainable solution, it is a valuable technology in the short to medium term due to abundant natural gas reserves and the increasing demand for H_2. Additionally, since this technology can use renewable natural gas from landfills and anaerobic digesters, it provides an ideal pathway for clean H_2 production in the long term.

As the need for clean, low-cost H_2 increases, the ideal technology roadmap for the proposed technology includes improvements to integrate and use renewable energy sources for heating and renewable feedstocks. To date, UND-CEMRI/Envergex proved that an "Electromagnetic Energy-Assisted Thermal Conversion of Fossil-Based Hydrocarbons to Low-Cost Hydrogen" can potentially represent a viable techno-economic process, able to compete with blue and green H_2 technologies. This step is represented in Figure 15 (I).

Future work will have to be focused on implementing the technology within the turquoise H_2 production sector (see (II) in Figure 15). A similar process has only recently been proven at large scale, with Monolith Materials in Nebraska operating the largest facility of its kind in the world since 2020.[7] This indicates that CH_4 pyrolysis is a viable pathway, and with additional research, the longevity of the catalysts that are used in these processes can potentially be extended to provide even greater energy efficiencies compared to SMR and electrolysis-based methods.

The third step in the technology roadmap will be to use electricity from renewable resources to yield green H_2 (see (III) in Figure 15). Since catalysts play a significant role in reducing the operating temperature of CH_4 decomposition, less energy-intensive methods like plasma-based reforming can be used to produce H_2, and the proposed catalyst reactivation technology will still apply to these processes.

The last step in the technology roadmap is expanding the catalyst cleaning technology into other industries that rely on catalysts that typically experience poisoning and deactivation (see (IV) in Figure 15). A prime example is within the fuels production industry, where cobalt catalysts can become deactivated by carbon during the Fischer-Tropsch synthesis reaction.[8] The proposed technology is potentially applicable to any process where catalyst deactivation occurs because of fouling.

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[7] https://monolith-corp.com/

[8] Argyle, M.D. and Bartholomew, C.H., 2015. Heterogeneous catalyst deactivation and regeneration: a review. *Catalysts*, 5(1), pp.145-269.

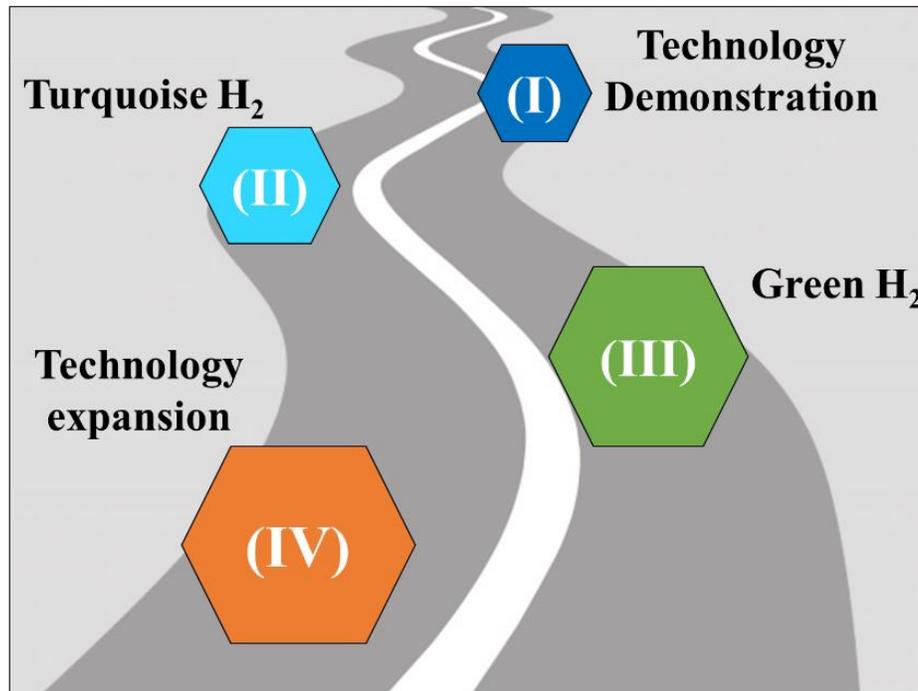**Figure 15:** Technology roadmap for electromagnetic energy-assisted thermal conversion of hydrocarbon feedstocks to low-cost H_2.

4. Budgetary Information

Table 2 outlines the cumulative expenditures for the project up to 07/31/2024.

Table 2: Cumulative expenditures.*

PROJECT EXPENDITURES			
Project Associated Expense	NDIC's Share for UND	NDIC's Share for Envergex	Total Project Cost
Total Personnel Expense	$ 27,573.69	$ -	$ 27,573.69
Total Operating Expenses	$ 14,727.19	$ 27,117.40	$ 41,844.59
Total Direct Cost	$ 42,300.88	$ 27,117.40	$ 69,418.28
Total F&A Expense	$ 17,343.33	$ 10,250.00	$ 27,593.33
Total	**$ 59,644.21**	**$ 37,367.40**	$ 97,011.61

* Note: Salaries and expenditures for the pay period ending 07/31/2024 are only posted on 8/15/24 and were therefore not included in this table.