Continuous Solar-Thermal Methane Pyrolysis by Roll-to-Roll Processing

Mostafa Abuseada Mechanical and Aerospace Engineering Department University of California Los Angeles California, USA mabuseada@ucla.edu

Abstract-Global warming concerns have motivated the study of new approaches that can decarbonize fossil fuels to produce clean fuels and commodities. A promising approach is solar-thermal methane pyrolysis to convert natural gas into clean hydrogen fuel and high-quality carbon product with virtually zero CO₂ emissions by utilizing concentrated solar power. However, one of the challenges to continuous methane pyrolysis is deactivation of catalyst, when present, and establishing a facile means of extracting the valuable carbon product. In this work, a scalable route to continuous solar-thermal methane pyrolysis is presented that employs a roll-to-roll mode of operation. A high-flux solar simulator is used to mimic concentrated solar power and to allow operation at temperatures of approximately 1500 K, where methane rapidly decomposes onto the fibers of a porous carbon roll, collecting graphitic solid carbon and exhausting clean hydrogen fuel in addition to unconverted methane. The efficacy of the roll-to-roll approach for methane decomposition is investigated, and the technique is observed to be effective in achieving a continuous process. The roll-toroll mechanism maintains stable and relatively high methane conversion compared to a stationary substrate, where enhancement in methane conversion as high as 42% is observed. The quality of the carbon product obtained is generally high, with Raman D/G peak ratios near 0.5. This work therefore establishes a proven baseline for continuous production of graphitic carbon from solar pyrolysis.

Keywords—Methane decomposition, Solar processing, Graphitic carbon production, Clean hydrogen, Roll-to-roll

I. INTRODUCTION

Global warming due to the continuing significant emission of greenhouse gases for energy, fuel, and commodity production threatens the Earth's climate stability. Heating processes, which represent 50% of global energy consumption [1], are currently driven mainly by combustion of fossil fuels with virtually no utilization of solar energy, which is the most abundant energy source and can be used in highly energyintensive processes through optical concentration [2].

In response to global warming concerns, the demand for hydrogen as a clean fuel and chemical building block [3] in addition to the demand for graphite for Li-ion batteries [4] has increased significantly over the past decade. However, hydrogen is currently predominantly produced through steam Timothy S. Fisher Mechanical and Aerospace Engineering Department University of California Los Angeles California, USA tsfisher@ucla.edu

methane reforming (SMR), which constitutes a highly endothermic reaction [5]. Likewise, carbon and graphite are predominantly produced through energy-intensive industrial processes, such as the furnace black process [6]. A promising alternative to producing these desirable commodities is methane pyrolysis [7], where methane breaks down essentially into hydrogen gas and solid carbon via the following simplified global dehydrogenation mechanism:

$$2CH_4 \xrightarrow{-H_2} C_2H_6 \xrightarrow{-H_2} C_2H_4 \xrightarrow{-H_2} C_2H_2 \xrightarrow{-H_2} 2C.$$
(1)

This reaction is energy-intensive and necessitates temperatures above 1300 K for satisfactory conversion. However, methane pyrolysis from solar energy leads to virtually no greenhouse gas emissions [8] and avoids emission of approximately 13.9 kg-equivalent $CO_2/kg H_2$ compared to conventional methods for hydrogen and carbon production (SMR and furnace black) [6]. Additionally, with production of high-quality carbon product, it has been projected that hydrogen can be produced at competitive costs [9].

Methane pyrolysis can be supplemented with a catalyst and via vacuum-aided decomposition. Although little prior work has investigated subatmospheric pressure conditions [7], product quality and yields per Le Chatelier's principle are expected to increase. As for processes supplemented with catalysts, they are generally divided into carbon-based and metal-based catalysts [10]. Compared to metal-based catalysts, carbonaceous catalysts generally offer the advantages of higher resistance to temperature, lower cost, and minimal post-processing methods to produce a sellable carbon product [11]. However, carbonaceous catalysts require higher operating temperatures and generally produce amorphous carbon [12], [13]. Both catalysts tend to undergo catalytic deactivation due to carbon production and deposition generally requires regular that catalyst regeneration/replacement [14], noting that carbonaceous catalysts undergo deactivation at much slower rates [15]. This deactivation challenge in addition to establishing an effective means of upgrading and extracting the solid carbon product hinders scalability to a continuous methane pyrolysis process.

Prior literature has considered relatively large-scale solar methane decomposition using various routes. Early studies report methane pyrolysis in volumetric/tubular solar reactors without a catalyst [16]. These processes generally require very high temperatures (1600-2100 K) and are thermally less efficient, and suffer from uncontained carbon production and

deposition that leads to window obstruction or tube clogging [17]. Other work investigated the use of carbon black catalysts in flow-seeded [18] or entrained-flow [19] solar reactors. However, flow obstruction from carbon deposition remains a challenge, and catalytic enhancement due to flow-seeding may not compensate for the added heating load of catalysts due to relatively short residence times [19]. Other studies report rotary-bed [20] and packed-bed [21] solar reactors that use carbonaceous and/or metal-based catalysts. Although metal-based catalysts enhance methane conversion and product quality, they suffer from sintering and rapid deactivation [20]. The use of molten metal alloys to mitigate catalyst deactivation and to allow for continuous methane pyrolysis was also investigated [22]. However, a significant portion of metal impurities (approx. 8%) may be present with the solid carbon product [23] that may typically requires additional purification. Establishing efficient carbon extraction and catalyst regeneration remains a challenge.

In recent work [8], we reported solar-thermal methane pyrolysis through a fixed carbon fibrous medium to coproduce high-quality graphitic carbon product and clean hydrogen fuel. Persistent high methane conversion and graphite growth/deposition rates were observed with direct concentrated solar irradiation and a locally heated reaction zone. The graphitic carbon was observed to grow conformally over the fiber ligaments, capturing almost the entirety of the carbon product in a readily extractable form [8]. However, flow blockage due to continuous growth and coalescing of fibers produced declining performance over time due to reduced residence time, reaction surface area, local gas flow, and active deposition sites. Therefore, in this study, a scalable route to solar-thermal methane pyrolysis into a continuous production process is reported by utilizing a roll-to-roll (R2R) mechanism. R2R has been utilized for continuous growth of graphene films [24] in addition to other materials, such as graphitic petals [25] and solar cells [26]. In this paper, the continuous solar-thermal pyrolysis process is presented, and the efficacy of the roll-to-roll approach for solar methane decomposition is quantified.

II. EXPERIMENTAL SETUP AND METHODOLOGY

The experimental setup consists of a light source that mimics concentrated solar radiation in a laboratory setting, a solar reactor, a R2R mechanism driving a fibrous carbon substrate, and *in situ* gaseous products monitoring systems that consist of a mass spectrometer (MS) and laser absorption spectroscopy (LAS) systems. An overview of the experimental setup and process are shown in Fig. 1. The concentrated light source brings a porous carbon roll to high temperatures locally, where pure methane (99.999% pure) enters the solar reactor and rapidly decomposes on the fibers of the carbon porous roll, depositing solid carbon and producing mainly hydrogen and unconverted methane in the product stream. The process performance is continuously monitored using the in-situ MS to quantify methane conversion in addition to hydrogen and carbon yields.

A. Solar Simulator and Reactor

The custom-built solar simulator system comprises a 10 kW_e xenon arc lamp, which is well-known to resemble the solar standard spectrum [27] that is supported and aligned at the first focal point of a silver-coated ellipsoidal reflector to concentrate its irradiation around the reflector's second focal point, as shown in Fig. 1. The lamp connects to a variable DC power supply to control its output power by varying the



Fig. 1. (a) Process overview of the roll-to-roll solar-thermal methane pyrolysis experimental setup. Figure inset in the top right shows photographs of the roll-to-roll mechanism and radiation shield. (b) Photograph of the experimental setup.

current supplied to the lamp within 100 to 200 A and to mimic transient variations in natural solar power if desired [28]. The solar simulator is additionally equipped with blowers and a pyrometer to maintain the thermal integrity of the solar simulator, and it is equipped with an automated gate that allows fully controlling the solar simulator via LabVIEW.

The irradiation output from the solar simulator onto the fibrous roll has been characterized using an inverse heat flux mapping method [29], giving a radially-symmetric heat flux distribution (q_s^r) that follows a pseudo-Voigt function:

$$q_{\rm s}''(r,I) = A_{\rm s}(I) \left[\frac{(1-\alpha_{\rm L})}{\sigma_{\rm G}\sqrt{2\pi}} \exp\left(\frac{-r^2}{2\sigma_{\rm G}^2}\right) + \frac{\alpha_{\rm L}}{\pi} \left(\frac{\sigma_{\rm L}}{r^2 + \sigma_{\rm L}^2}\right) \right] \quad (2)$$

where *I* is the supplied current to the lamp, *r* is the radius from center, the weighing coefficient is $\alpha_{\rm L} = 0.519$, the Lorentzian and Gaussian distribution parameters are $\sigma_{\rm L} = 0.0492$ m and $\sigma_{\rm G} = 0.00829$ m, and the amplitude parameter is $A_{\rm s} = 0.740I - 20.5$ kW/m. Using Eq. (2), the heat flux and cumulative power distributions are plotted for a supply current value of 160 A as shown in Fig. 2.

The solar reactor, shown in Fig. 1, consists of a large coldwall stainless steel cylindrical chamber with an overall height of 40.6 cm and inner diameter of 30.5 cm. The chamber walls are cooled via embedded water lines, and cooling is supported using a 1.4 kW chiller. A 12.7 mm thick quartz that is 25.4 cm in diameter is used to seal the reacting flow while allowing direct irradiation from the solar simulator onto the carbon fibrous roll. To maintain the thermal integrity of the quartz window and avoid unwanted carbon deposition, the quartz window is supported by a water-cooled flange and is additionally cooled using a blower. The solar reactor also has a total of seven additional ports. Four of these ports are located at 90° angles from the focal plane (where the carbon roll is located) and interface with an upstream capacitance manometer, motors for the roll-to-roll mechanism, and the inlet feedstock line. Furthermore, two ports are located at a 45° angle from the focal plane to allow optical access to the top side of the roll, where a high-resolution longwave infrared (IR) camera measures temperatures up to 2100°C and monitors front side spatial temperatures. The IR camera was calibrated to the fibrous material and viewports against a Ktype thermocouple, leading to an apparent emissivity of 0.9 and an uncertainty of 30 K for temperatures reported in this



Fig. 2. Local and average heat flux distributions and cumulative power from the solar simulator onto the carbon roll for a supply current of 160 A.

study [8]. The last port (3.8 cm in diameter) is located directly below the roll to serve as the reactor's exhaust and to allow monitoring the roll's temperature from the rear side.

The R2R mechanism, shown in Fig. 1, is custom built from stainless steel and allows for a roll width of 3.8 cm, where the processed region of the roll is always located within the focal plane of the reactor and solar simulator. One side of the mechanism is used to store the carbon roll prior to experimentation, where two independent stepper motors are used to drive the roll from the loaded side to the empty side while maintaining the roll's proper tension. Moreover, an annular disk with circular aperture of 3.8 cm gently applies additional tension on the roll's reaction zone to minimize flow bypass through the exhaust line, and a stainless steel radiation shield protects the roll-to-roll mechanism and its auxiliaries.

B. Process Monitoring

The product stream of the solar reactor is directed through *in situ* monitoring systems, as shown in Fig. 1. A detailed description of the systems and techniques are presented elsewhere [8], where the MS has been calibrated for the five more prevalent gas species present in the product stream; these species consist of H₂, CH₄, C₂H₂, C₂H₄, and C₂H₆. Having the mole fractions of species *i* in product stream (x_i) identified and methane inlet flow rate controlled, the molar flow rate out of the reactor (\dot{n}_{out}) in addition to the carbon production rate (m_c) can be determined from hydrogen and carbon balance as [8]:

$$\dot{n}_{\text{out}} = \frac{2\dot{n}_{\text{in}}}{x_{\text{H}_2} + 2x_{\text{CH}_4} + x_{\text{C}_2\text{H}_2} + 2x_{\text{C}_2\text{H}_4} + 3x_{\text{C}_2\text{H}_6}},\qquad(3)$$

$$\frac{\dot{m}_{\rm C}}{M_{\rm C}} = \dot{n}_{\rm in} - \dot{n}_{\rm out} \left(x_{\rm CH_4} + 2x_{\rm C_2H_2} + 2x_{\rm C_2H_4} + 2x_{\rm C_2H_6} \right).$$
(4)

Methane conversion (X_{CH_4}) in addition to the overall hydrogen (Y_{H_2}) and carbon (Y_C) yields are determined as:

$$X_{\text{CH}_4} = \frac{\dot{n}_{\text{in}} - \dot{n}_{\text{out}} x_{\text{CH}_4}}{\dot{n}_{\text{in}}} ; Y_{\text{H}_2} = \frac{\dot{n}_{\text{out}} x_{\text{H}_2}}{2\dot{n}_{\text{in}}} ; Y_{\text{C}} = \frac{\dot{m}_{\text{C}}}{M_{\text{C}}\dot{n}_{\text{in}}} .$$
 (5)

C. Materials and Characterization Techniques

The carbon roll starting materials used in this study consist of carbon felts and cloths. The carbon felt (FuelCellEarth, C200) is comprised of nonwoven polyacrylonitrile-based carbon fibers of 10 µm nominal diameter with an estimated effective porosity of 0.952 and relatively low specific surface area $(1.5 \text{ m}^2/\text{g})$ [8]. In contrast, the carbon cloth (FuelCellEarth, CC6) is comprised of woven carbon fibers of 8.7 µm nominal diameter with an estimated effective porosity of 0.82. Both the carbon felt and cloth are resistant to high temperature decomposition. For solid carbon characterization, scanning electron microscope (SEM) images were captured by a ZEISS Supra 40VP field emission SEM with a secondary electrons detector and energy dispersive X-ray spectroscopy (EDS) detector, Raman spectra were obtained using a 532 nm laser with a $40 \times$ achromatic objective lens and a CCD detector of a Horiba iHR 550 imaging spectrometer, and Xray diffraction (XRD) spectra were measured by a Panalytical X'Pert Pro X-ray powder diffractometer with a Cu K α source.

III. RESULTS AND DISCUSSION

A. Process Performance

A series of tests were conducted at various operating conditions implementing the use of the developed roll-to-roll mechanism to investigate its efficacy for solar-thermal methane pyrolysis. For testing, the solar reactor is evacuated while purging with nitrogen to ensure an oxygen-free environment. Solar insolation then begins at vacuum condition, where pure methane flow is introduced to the solar reactor at the tested flow rate. Gaseous product monitoring data using the *in situ* MS was used to determine transient methane conversion and product yields as presented in Fig. 3, where the solar power is estimated by integrating Eq. (2) over the unshielded area (63.5 mm in diameter).

The first test (Roll 1, Fig. 3a) was conducted using the carbon cloth (CC6) with a thickness of 0.89 mm at operating pressure of 25 Torr, solar power of 1.78 kW (160 A), and with methane inlet flow rates of 200 and 400 sccm. The estimated reaction residence times through the thickness of the cloth at these flow rates are 37 and 19 ms, respectively, with an average temperature of 1470 K on the cloth subject to solar irradiation. As shown in Fig. 3a, methane conversion and product yields decrease when the roll is stationary at both flow rates tested. This reduction is due to progressive deposition of graphitic carbon on the roll's fibers that leads to flow obstruction and reduced residence times [8]. However, when the carbon roll is moved to a fresh region and remains rolling, the methane conversion and product yields significantly increase and approach maximum values without flow obstruction. At 200 sccm, methane conversion increases from 42% to 51% upon rolling, while it increases from 31% to 37% at 400 sccm. Similarly, hydrogen and carbon yields undergo similar enhancements, where the improvement in stationary performance should increase with the decomposition duration. However, due to the combination of flow rate, solar power, and roll thickness, methane conversions and product yields are moderate, and are expected to improve upon mitigation of issues such as flow bypass around the porous carbon roll and optimization of thermodynamic conditions.

The second test (Roll 2, Fig. 3b) was performed on a carbon felt (C200) with a thickness of 6.35 mm at pressure of 25 Torr, solar power of 1.78 kW, and inlet flow rates of 500 sccm and 1000 sccm. The resulting average temperature of the felt under solar insolation was 1520 K. As a result of increase in roll thickness, the performance benefits from higher flowrates due to the increase of the reaction zone thickness, where residence times at 500 and 1000 sccm are 118 and 59 ms. The enhancement in process performance upon rolling the carbon felt is similar to that observed for Roll 1 (Fig. 3a), with 21% and 27% increases in methane conversion at 500 and 1000 sccm. However, in contrast to the thin carbon cloth, the thick felt rolls less easily.

Two additional tests were conducted to assess the influence of web speed and its effect on the pyrolysis process while further demonstrating the capability of the roll-to-roll mechanism at higher solar powers. A carbon cloth (CC6) with a thickness of 0.89 mm (Roll 3, Fig. 3c) was tested at pressure of 25 Torr, solar power of 2.23 kW (190 A), and inlet flow rate of 200 sccm, with web speeds of 2, 3, and 4 mm/min. The carbon web requires rolling for a distance of 3.8 cm to fully replace the starting roll section. Methane conversion as high as 68% was observed at the maximum web speed with at average temperature and residence time of 1580 K and 35 ms, where the steady-state process performance enhances with higher web speed. However, the change in steady-state conversion and yields was relatively small beyond web speeds of 3 mm/min.



Similarly to initial testing, Roll 3 exhibits enhanced

Fig. 3. Experimental testing of roll-to-roll solar-thermal methane pyrolysis demonstrating effective operation at four operating conditions quantified via conversion and yields. Testing at operating pressure of 25 Torr and (a) power of 1.78 kW and thickness of 0.89 mm (b) power of 1.78 kW and thickness of 6.35 mm (c) flow rate of 200 sccm, power of 2.23 kW, and thickness of 0.89 mm, (d) flow rate of 200 sccm, power of 2.15 kW, and thickness of 1.78 mm.

methane conversion as high as 42% when comparing the performance of a rolling cloth to a stationary one. Another carbon cloth with a thickness of 1.78 mm (Roll 4, Fig. 3d) was tested at pressure of 25 Torr, solar power of 2.15 kW (185 A), and inlet flow rate of 200 sccm. Roll 4 yielded similar results to those of Roll 3, but with higher methane conversion up to 76% due to the increased residence time (69 ms) despite the slight reduction in solar power. Hydrogen and carbon yields were significantly higher and closer to the methane conversion as a result of presence of less minor hydrocarbons (mainly C_2H_2) in the product stream due to more complete dissociation. In contrast to Roll 2, the reduced thickness of Roll 4 enabled it to roll smoothly.

B. Carbon Product

The quality of the carbon product generated during testing of the four rolls is presented in Fig. 4, where SEM images indicate that the graphitic carbon product conformally grows over the starting fibers. Comparing graphitic growth of the roll's fibers using SEM images, the original cloth fibers (Fig. 4a) are observed to undergo significant growth under short processing time. The fibers in Rolls 1, 3, and 4 (Fig. 4b-d) are grow up to 5.5 times their initial diameters. EDS spectra of the carbon product were obtained (not shown) because they revealed only single atomic carbon peaks, indicating the high purity of the carbon product as expected from an oxygen-free environment. Comparing Rolls 1 and 4, fibers in Roll 1 exhibit more irregularities and slightly rougher deposition due to the nonideal pyrolysis conditions (i.e., lower solar power and residence time). To characterize the graphitic product further, an SEM image of a cross-sectional cut of one of the fibers of Roll 2 is shown in Fig. 4e, which demonstrates the significant growth of the original fibers in addition to the formation of microporous graphitic layers [8].

The carbon product was further characterized by obtaining Raman (Fig. 4f) and XRD spectra (Fig. 4g). Raman D, G, and

2D peaks are present and narrow, indicating the production of relatively high-quality carbon product in contrast to the weak/missing Raman 2D peak in the original starting material and amorphous carbon generally produced in prior literature by carbonaceous catalysts [30]. A similar observation applies to the XRD spectra, where literature shows missing distinct XRD peaks for the amorphous product generated [20]. Consistent with the SEM images, Roll 4 produced a much higher quality carbon product compared to Roll 2, where the D/G peak ratio is 0.49 (compared to 1.16). XRD spectra also complement the Raman spectra and indicate the presence of a relatively high-quality graphitic product with a distinct and narrow (002) peak. The peak occurs at a 2θ of approximately 25.9°, which corresponds to an average interplanar distance of 0.343 nm using Bragg's law [31], compared to 0.335 nm for perfectly crystalline graphite. Moreover, the graphitic quality is expected to improve further with process optimization.

IV. CONCLUSIONS AND FUTURE WORK

In this work, the use of roll-to-roll mode of operation for continuous solar-thermal methane pyrolysis is presented. A solar simulator is used to mimic concentrated solar power, allowing operation at temperatures of approximately 1500 K. Methane is observed to rapidly decomposes onto the fibers of a porous carbon roll, trapping graphitic solid carbon and exhausting clean hydrogen fuel. The roll-to-roll approach for methane decomposition is observed to be effective in achieving a continuous process, where it maintains stable and relatively high methane conversions compared to a stationary substrate with enhancement in methane conversion as high as 42%. The quality of the carbon product obtained is generally high, with Raman D/G peak ratios as low as 0.49. With additional process and design optimization, such as by using a secondary concentrator, the process performance and product quality are expected to enhance significantly.



Fig. 4. Characterization results of solid carbon product of the four different experimental roll-to-roll tests. SEM images for: (a) original carbon cloth/roll, (b) Roll 1 experiment, (c) Roll 3 experiment, (d) Roll 4 experiment, and (e) Roll 2 experiment. (f) Raman and (g) XRD spectra of the roll-to-roll original carbon cloth and carbon product generated in different tests.

DECLARATION OF COMPETING INTEREST

TSF is co-founder of a company (SolGrapH Inc.) that is involved with solar-thermal material synthesis. The submitted work is an academic study outside the scope of this activity and is not intended or represented as a commercial product or promotion.

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