# Hydrogen Production from Methane Pyrolysis

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Methane pyrolysis process involves decomposition of natural gas (NG)/methane at extremely high temperatures (T >1100 °C) in the absence of air to produce hydrogen, carbon black and small amount of coke. The overall reaction mechanism is shown in the equation below.

$$CH_4 \xrightarrow{Heat} C_{solid} + 2H_2$$

Carbon black is produced in the highest quantity with approximately 72.1% share by mass, followed by hydrogen with 27.8%, and coke with 0.1%, respectively. Carbon black is commonly used in the production of tires, vehicle upholstery, and in the coloring industry as pigments. Additionally, steam is generated through the excess heat recovery in the process which has the potential for export. A schematic diagram for the methane pyrolysis process is shown in Figure 1.

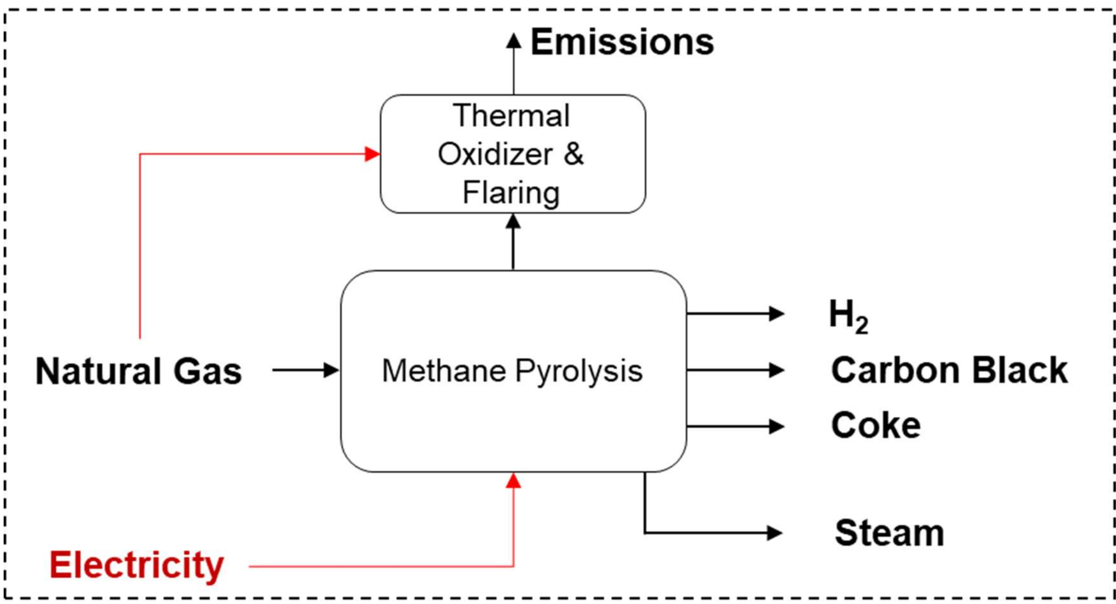


Figure 1: Schematic diagram for methane pyrolysis process. Red arrows indicate fuel/utility.

Conventionally, hydrogen is produced via steam methane reforming (SMR) and autothermal reforming (ATR) of natural gas. However, the carbon present in the natural gas using these technologies has been conventionally released in the form of $CO_2$ to the atmosphere. To reduce the $CO_2$ emissions from SMR and ATR, $CO_2$ capture and sequestration (CCS) technology is used. Methane pyrolysis avoids the need for CCS because almost all the carbon in natural gas is converted to solid carbon black and coke, with a small amount of $CO_2$ released onsite via flaring and thermal oxidizer (TO) emissions. The pyrolysis process requires high temperature conditions which may be achieved through an electric heater, thereby making it an electric-intensive process. In that case, the key contributing factor to the greenhouse gas (GHG) emissions of methane pyrolysis process is the carbon intensity (CI) of sourced electricity. Table 1 shows the process inputs and output for the methane pyrolysis process in GREET 2023.

Table 1: Process inputs and outputs for hydrogen production via methane pyrolysis.

| Methane Pyrolysis | Components | Value | Units* (per mmBtu $H_2$) |
|---|---|---|---|
| Inputs | NG | 1.733 | mmBtu |
| | Electricity | 328.4 | kWh |
| | Other Input (Diesel) | 0.450 | mmBtu |
| | Process Water | 26.24 | gal |
| Outputs | Carbon Black | 0.867 | mmBtu |
| | Coke | 0.027 | mmBtu |
| | Steam (50 bar, 265°C) | 0.275 | mmBtu |

*Energy units are on lower heating value basis. Steam energy output value is determined based on enthalpy difference with water at 1 bar and 25°C.

Diesel is considered as a surrogate to account for the upstream emissions associated with undisclosed inputs and was decided based on carbon balance of the facility; its impact on the allocated emissions is significantly small, as shown in Figure 3. Most of the carbon embedded in NG is converted to carbon black or coke. The remaining amount (relatively small) is emitted from the facility through thermal oxidizer and flaring. The emission profile for both the technologies normalized over NG feedstock input is provided in the Table 2.

Table 2: Emission profile for thermal oxidizer and flaring technology.

| Component | Thermal Oxidizer Emissions (g/mmBtu NG) | Flare Emissions (g/mmBtu NG) |
|---|---|---|
| CO | 0.146 | 0.016 |
| $CO_2$ | 4,207 | 75 |
| $H_2$ | - | - |
| $H_2O$ | 3,843 | 43 |
| $NO_2$ | 0.382 | - |
| $N_2$ | 22,581 | - |
| $O_2$ | 0.188 | - |
| $CH_4$ | 0.080 | 0.264 |
| $C_2H_6$ | 0.009 | 0.031 |
| $C_3H_8$ | 0.002 | 0.005 |
| $C_4H_{10}$ | - | 0.001 |

In GREET 2023, three allocation methods (mass allocation, energy allocation and market value allocation) are implemented as allocation options for energy use and emissions associated with the methane pyrolysis main products (carbon black, hydrogen, coke). Before applying allocation method, displacement credit may be provided for the co-produced steam if valorized through export to adjacent markets, otherwise steam may not be treated as a co-product (i.e., considered a waste product). The mass allocation is the default approach adopted in GREET to allocate the process emissions between hydrogen and solid carbon black products, since the latter is not conventionally used for its energy value, while steam co-product displacement credit is provided by default assuming its export. Example of allocation factors is provided in Table 3 assuming displacement credits for steam export. Emissions associated with production of hydrogen, carbon black and coke based on mass, energy and market value (MV) allocation options are shown in Figure 2.

Table 3: Allocation factors (AF) based on mass, energy, and market value in methane pyrolysis process

| **Products** | **Normalized Output per kg $H_2$** | **Mass AF** | **LHV (MJ/kg)** | **Energy AF** | **Estimated market value ($/kg)** | **MV AF** |
|---|---|---|---|---|---|---|
| $H_2$ | 1 | **21.83%** | 120 | **52.8%** | 1.2 | **15.4%** |
| Carbon Black | 3.47 | **75.75%** | 30[1] | **45.8%** | 1.9[2] | **83.9%** |
| Coke | 0.11 | **2.42%** | 29[3] | **1.4%** | 0.5[4] | **0.7%** |

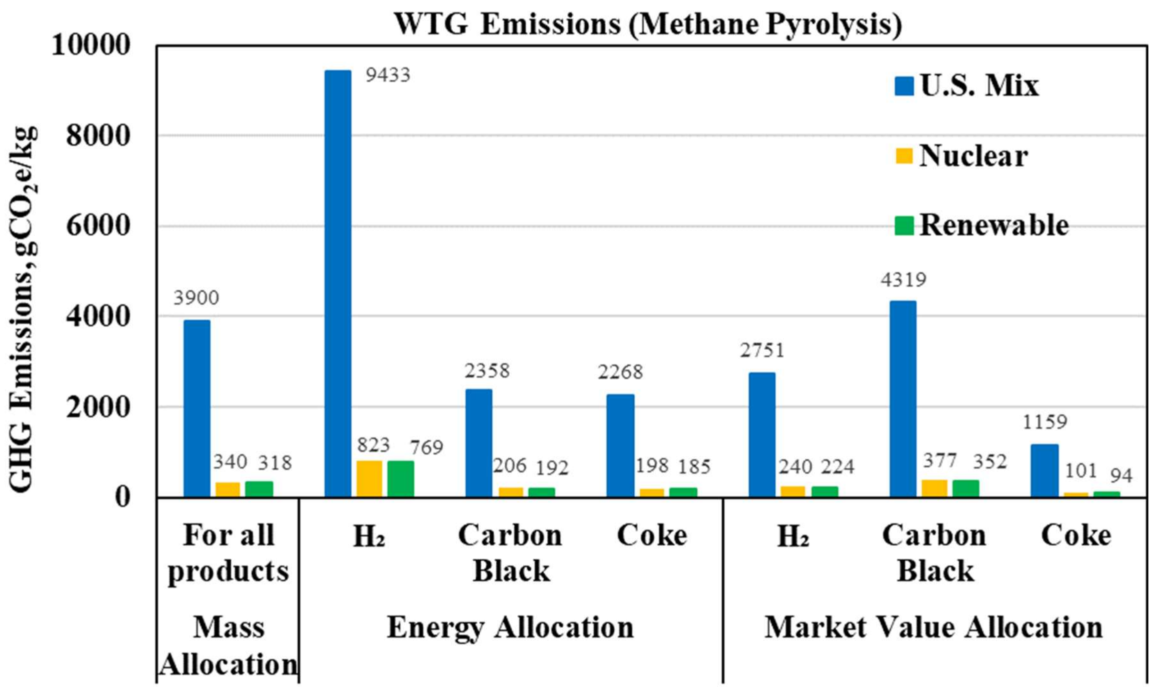


Figure 2: WTG emissions for methane pyrolysis products based on various allocation methods. Displacement credits for steam is assumed and mass allocation is used by default in GREET 2023

The default well-to-gate (WTG) GHG emission of $H_2$ produced from methane pyrolysis process in GREET 2023 is estimated at 3.9 kg$CO_2$e/kg $H_2$. The displacement credits associated with steam export are 0.62 kg$CO_2$e/kg $H_2$. Approximately 3.6 kg$CO_2$e/kg $H_2$ of the total GHG emissions in methane pyrolysis is due to the CI of electricity supplied (assuming 2023 US grid mix[5]) as shown in Figure 3. If a cleaner electricity source is used (i.e., nuclear or renewable power) for methane pyrolysis, the WTG GHG emissions of produced hydrogen reduces to 0.34 kg$CO_2$e/kg $H_2$ and 0.32 kg$CO_2$e/kg $H_2$, respectively.

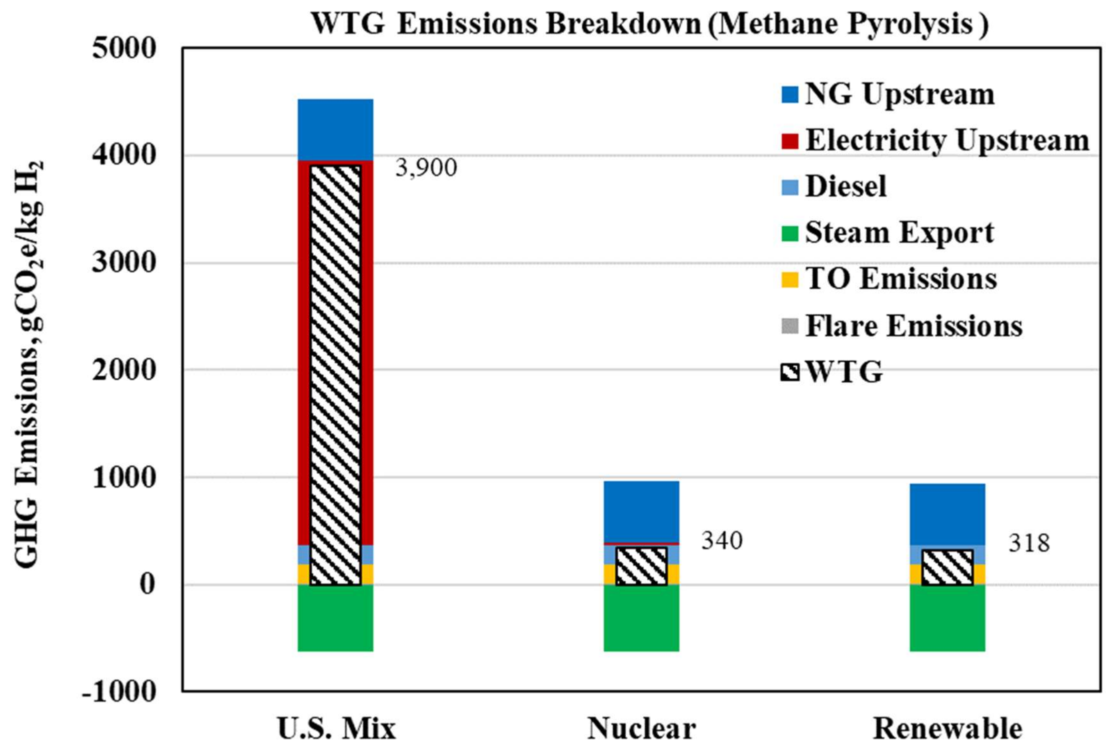


Figure 3: WTG emissions breakdown for methane pyrolysis process based on mass allocation (with steam displacement credits).

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