1

Why Do We Care About Methane?

1.1 Chemical Production

Methane (CH_4) plays a significant role in two key sectors: chemical production and energy supply. It is anticipated to emerge as a substitute for petroleum, serving as a foundational raw material in chemical industries. Over the last decades, the maturation of shale gas extraction techniques, such as horizontal drilling and hydraulic fracturing, has significantly lowered the cost of shale gas. Consequently, the usage of CH_4 as a raw material in the production of intermediate compounds has increased in the past decade, although presently, the primary raw material for chemical and manufacturing industries is still petroleum.

One of the major applications of CH_4 is the production of H_2 at an industrial scale through steam reforming for chemical production, food processing, and fertilizer synthesis. Other than these conventional applications, industries have increasingly turned to CH_4 to produce chemical intermediates, thereby creating value-added chemicals for manufacturing industries, although petroleum is still the dominant raw material for years or even decades. CH_4 can undergo chemical transformation through syngas route and direct transformation routes (Figure 1.1). In direct pathways, CH_4 is converted into synthesis gas (a mixture of CO and H_2) via steam reforming, dry reforming, or partial oxidation. Synthesis gas serves as a precursor to numerous vital intermediate compounds of chemical industries, including methanol, hydrocarbons, hydrogen, and many others. These intermediate can be used to produce a great number of value-added chemicals such as acetic acid, formaldehyde, vinyl acetate, allyl alcohol, alkylbenzene, propylene oxide, ethanol, acrolein, ethyl chloride, other alcohols, Hydrogen peroxide, alkylamine, aniline, nitrile, and ammonia. These value-added chemicals serve as building blocks for manufacturing various functional materials, including plastics, polymers, cloths, cosmetics, and medicines (Figure 1.1).

Particularly noteworthy is the routes of chemical production from CH_4 that avoids releasing environmentally harmful CO_2. Unfortunately, most CH_4 transformation reactions listed in Figure 1.1 occur at high temperatures, demanding substantial energy input, costly production facilities, and extensive maintenance. Furthermore, many of these transformations yield CO_2 as a byproduct. Particularly noteworthy are these routes of chemical

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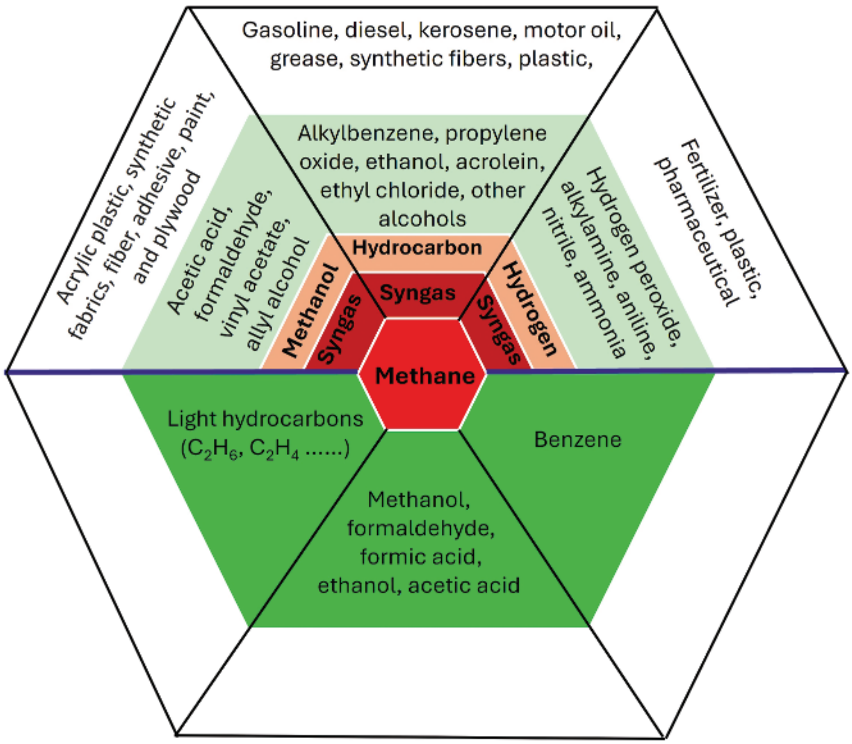

Figure 1.1 Expected chemical transformation map taking CH_4 as a substitute for petroleum in synthesizing crucial chemical intermediates to produce value-added chemicals and materials used in healthcare and daily household products.

production from CH_4 that do not release environmentally harmful CO_2. Therefore, the development of low-temperature reactions without releasing CO_2 and suitable catalysts for these reactions is vital to achieve a green transformation of CH_4 with low energy input and zero environmental impact. This pursuit underscores the significance of fundamental studies of activation and catalytic transformation of CH_4 under a mild condition in terms of low reaction temperatures.

1.2 Energy Supply

In the energy sector, CH_4 presently contributes predominantly to electricity generation [1]. The combustion of CH_4 at high temperatures provides heat to vaporize water, generating steam to drive electrical generators in CH_4 power plants. The advent of shale-gas-based electricity generation has considerably reduced electricity prices, leading to the retirement of numerous coal plants in America. According to the United States Energy Information Administration, 39.8% of electricity in the United States is generated through CH_4 combustion-based power plants (Table 1.1) [2]. It is the largest component in fossil-fuel-derived electricity, including 39.8% from CH_4, 19.5% from coal, and 0.6% from petroleum.

Table 1.1 The US utility-scale electricity generation by source, amount, and share of the total in 2022 (data as of October 2023).[a]

Energy source (Category level 1)	Energy source (Category level 2)	Energy source (Category level 3)	Amount (kWh)	Share of total
All sources			4231	**100%**
Fossil fuels (total)			**2553**	**60.4%**
	Natural gas		1687	39.9%
	Coal		832	19.7%
	Petroleum (total)		23	0.5%
		Petroleum liquids	16	0.4%
		Petroleum coke	7	0.2%
	Other gases[b]		12	0.3%
Nuclear	**Nuclear**		**772**	**18.2%**
Renewables (total)			**901**	**21.3%**
	Wind		434	10.3%
	Hydropower		255	6.0%
	Solar (total)		144	3.4%
		Photovoltaic[c]	141	3.3%
		Solar thermal	3	0.1%
	Biomass (total)		52	1.2%
		Wood	35	0.8%
		Landfill gas	9	0.2%
		Municipal solid waste	6	0.1%
		Other biomass waste	2	<0.1%
	Geothermal		16	0.4%
Pumped storage hydropower[d]			**−6**	**−0.1%**
Other sources[e]			**11**	**0.3%**

[a] Utility-scale electricity generation is electricity generation from power plants with at least 1 MW (or 1000 kW) of total electricity generating capacity. Data are for net electricity generation.
[b] Small-scale solar photovoltaic (PV) systems are electricity generators with less than 1 megawatt (MW) of electricity generating capacity, which are not connected to a power plant that has a combined capacity of one MW or larger. Most small-scale PV systems are at or near the location where the electricity is consumed, and many are net metered systems. Smaller PV systems are usually installed on building rooftops.
[c] Other gases include blast furnace gas and other manufactured and waste gases derived from fossil fuels.
[d] Pumped storage hydroelectricity generation is negative because most pumped storage electricity generation facilities use more electricity than they produce annually. Most pumped storage systems use fossil fuels or nuclear energy for pumping water to the storage component of the system.
[e] Other (utility-scale) sources include nonbiogenic municipal solid waste, batteries, hydrogen, purchased steam, sulfur, tire-derived fuel, and other miscellaneous energy sources.
Source: [2] / U.S. Energy Information Administration / Public Domain.

In addition, nuclear power plants and renewables contribute 18.2% and 21.5%, respectively. Essentially, CH_4, coal, nuclear, and renewables account for 39.8%, 19.5%, 18.2%, and 21.5% of the electricity generated in the United States (Table 1.1) [2].

Apart from electricity generation for industries and households, CH_4 serves as the primary energy source for three energy-end uses, including space heating, water heating, and cooking for households across the United States (Figure 1.2). As per the 2020 report from the United States Energy Information Administration, 61% of households in the United States utilize natural gas for at least one energy-end use [3]. As shown in Figure 1.2, the Midwest Census Region and West Census Region have the highest share of households at 74% in 2020. The share of households for spacing heating, water heating, and cooking in the South was lowest.

In certain European and Asian countries, CH_4 is allowed to directly be employed as fuel to combust in natural gas engines for vehicles, while it remains prohibited for combustion engines in North American. Consequently, CH_4 serves as the fuel for methane-powered vehicles in these regions. In addition, CH_4 is utilized in emergency hospital situations to generate electricity through high-temperature fuel cells [4]. As shown in Figure 1.1, the syngas derived from CH_4 can be employed in producing gasoline through the Fischer–Tropsch synthesis. However, this route is neither cost-competitive in contrast to gasoline production of petroleum refineries nor environmentally friendly [5].

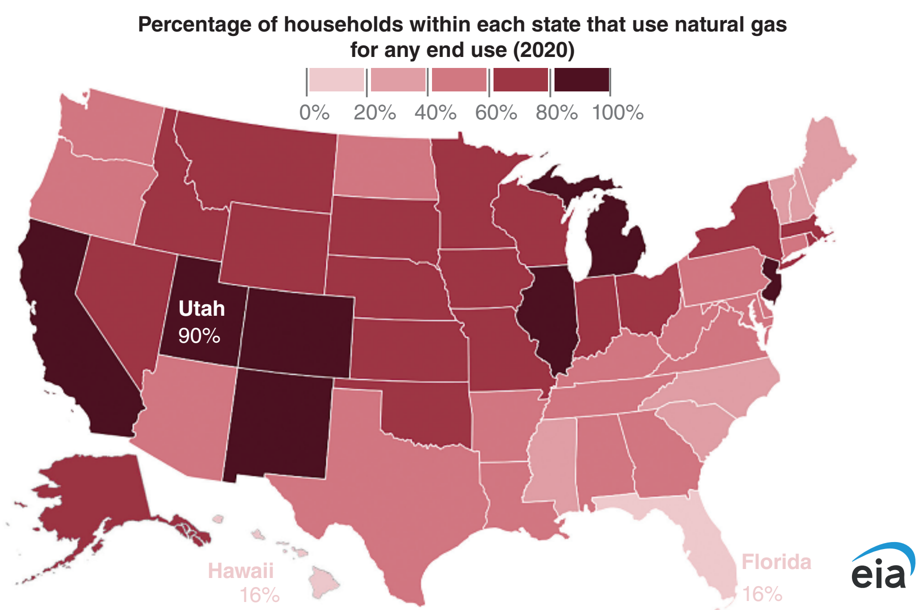

Figure 1.2 Percentage of households within each state that use natural gas for any end use in 2020. *Source:* Reproduced with permission from U.S. Energy Information Administration, Residential Energy Consumption Survey [3] / U.S. Energy Information Administration. All words and percentages in the figure were added by the source of this figure.

1.3 Climate Change

The utilization of CH_4 has resulted in a significant environmental challenge concerning the greenhouse gas effect [6, 7]. The 2016 Paris Agreement established a goal aimed at curbing climate change, specifically limiting the global average temperature increase to well below 2 °C above preindustrial levels. This legally binding international treaty, adopted by 196 countries worldwide, came into effect on 4 November 2016. The objective was described as restricting global warming to an increase of 1.5 °C by the end of this century. To achieve this goal, global emissions by 2030 need to be halved from the 2010 emission levels, with emissions reaching net zero by 2050.

CH_4, in terms of the greenhouse effect, holds a potency 26 times greater than that of carbon dioxide. As briefed above, the Global Methane Pledge was introduced during the 26th Conference of the Parties (COP-26) in Glasgow in November 2021 to address CH_4 emissions [8]. This pledge garnered endorsement from 111 countries, committing to collaborating to reduce CH_4 emissions by 30% of the 2020 levels by 2030 [8, 9]. The pledge sets forth an ambitious reduction within a mere nine years, expected to lead to a net cooling effect within a decade. It stands as the first international policy commitment solely addressing CH_4 emissions.

Unfortunately, CH_4 emission sources span a wide spectrum, ranging from coal mines, wetlands, petroleum industries, power plants, nonelectric vehicles, and biomass burning to ruminant digestion in livestock. Understanding the formation of CH_4 from anthropogenic activities and its subsequent emission into the atmosphere is crucial in minimizing CH_4 emissions and ensuring the environmentally friendly utilization of CH_4 derived from these activities. This underlines the critical importance placed on CH_4 within our environmental concerns. Chapters 3 and 5 discuss the formation of CH_4 and its emission to the atmosphere, respectively.

1.4 Reconciling Shale-Gas Utilization and Environmental Issue

The utilization of CH_4 in chemical and manufacturing industries revolves around its fundamental roles as a raw material for producing essential intermediate compounds of chemical industries for manufacturing functional materials for our daily life – such as plastics, rubber, textiles, cosmetics, fertilizers, and medicines – and as a source of hydrogen (H_2) for various chemical processes and material manufacturing. In the carbon cycle, CH_4 plays a vital role unless existing carbon-containing materials can be efficiently recycled to meet the demand for chemical and functional materials without requiring additional carbon sources. Achieving such an ideal carbon cycling world would necessitate the development of a comprehensive array of recycling techniques, with economic feasibility being a key determinant of their adoption. While it is conceivable that future industries may rely solely on recycling existing carbon-containing chemicals and materials without extracting additional raw materials from shale gas, it is not sure when such a transition could be accomplished.

In the interim, until sustainable recycling-based chemical and manufacturing industries are realized, the substitution of petroleum with natural gas remains an option. Biomass also presents an alternative source of carbon-based chemicals, but the portion of its application to consumable carbon-containing materials is still temporarily limited for the issue of costs and other reasons. Therefore, from the perspective of chemical production and material manufacturing, CH_4 is expected to maintain a certain share in an unknown period of time.

CH_4 emission is one of the major contributors to global warming. CH_4 emission primarily stems from leaks at shale gas production sites. Mitigating CH_4 emissions can be achieved by employing technologies such as green completions or reduced-emissions completions, which can reportedly reduce leaked CH_4 by up to 90% [10]. Addressing the impact of CH_4 emissions on climate change necessitates strategies such as isolating wells and implementing leak prevention measures. However, a long-term solution to minimize the contribution of CH_4 to global warming involves transitioning the current energy supply system towards a cleaner alternative, such as an optimized composite energy system consisting of nuclear energy and various forms of renewable energies such as wind, hydropower, solar, biomass, and geothermal energy.

Nevertheless, the transition to a cleaner energy system does not imply the elimination of shale gas from either industries or our daily lives. Compared to petroleum and coal for chemical and manufacturing industries, CH_4 is often a preferable raw material. This transition towards cleaner energy sources is expected to occur and last over decades, during which CH_4 is likely to continue contributing to the energy sector. Balancing the anticipated utilization of CH_4 in chemical and manufacturing industries with its contribution to global warming requires stringent policies to manage CH_4 emissions, technological advancements in shale gas drilling with minimal leak and zero environmental impact, and the development of new catalytic processes for transforming CH_4 into value-added chemicals with low-energy cost and zero CO_2 emission under mild conditions in terms of a reaction temperature of room temperature or low temperature (25–250 °C). Therefore, it is significant to develop efficient, green transformations of CH_4 into highly valued intermediate compounds for chemical and manufacturing industries, such as methanol and acetic acid, under mild conditions. The global community has made significant strides in this direction in the last decade, with ongoing efforts focusing on room temperature and low-temperature activation and catalytic transformation of CH_4 into value-added chemicals, as discussed in the following chapters.

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