



Utilization of CO₂ for Methanol Synthesis from Coal- Fired Power Plant

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Abstract. This paper describes a first-of-its-kind Flue Gas CO₂ to Methanol (FG-CTM) Demonstration Plant that has been developed to capture carbon dioxide from the flue gas of a fossil-fuel-based power plant and convert it into methanol through catalytic hydrogenation. The integrated system comprises three major process blocks: (i) CO₂ Capture, (ii) Hydrogen Generation via electrolysis, and (iii) Methanol Synthesis. This demonstration aims to establish the techno-economic feasibility of CO₂ capture and utilization (CCU) technologies in the context of coal-fired power generation. The methanol sample obtained from the stripper section and analyzed using gas chromatography technique showed 99.85% purity conforming to ASTM Grade A methanol.

Keywords: Carbon Capture and Utilization (CCU), Thermal Power, Methanol Synthesis, Proton exchange membrane (PEM) electrolyzer, CO₂ to Methanol.

1 Introduction

CO₂ emissions from fossil fuel use, are a major cause of global warming and a major part of fossil fuel is used for electricity generation. As per the report of Central Electrical Authority of India [1], the percentage share of electricity generation plant capacity by solar PV will increase from 16% in 2023 to 38% in 2030, and the percentage share of electricity generation plant capacity by coal and lignite will drop from 51% to 32%. In India, the installed capacity of electricity generation in 2023 is around 418 GW and it will become 777 GW in 2030. Although there is a decrease in the share of electricity generation plant capacity by coal and lignite, there will 19% increase in electricity generation plant capacity from 2023 to 2030, which will lead to an increase in the CO₂ emissions. To achieve net zero emissions, the first step is to reduce the CO₂ emissions per unit of power generation to the level of Combined Cycle Gas Turbine CO₂ emission which is around 490 g/kwh. The present CO₂ emission level of coal and lignite power plants is around 938 g/kwh [1].

For long-lasting growth of industry energy security, energy affordability, and energy sustainability are important; to achieve these targets there are two methods. The first method is to blend green fuel in coal and the proportional amount of CO₂ emissions will be considered as a reduction in CO₂ emissions. The second method is CO₂ capture from flue gas. In the first method, 10% blending of biofuel pellets in coal-fired boiler is achieved and the feasibility of coal-fired boiler operation with 20% biofuel pellet blending is under investigation [2]. In second method, the captured CO₂ should be either stored or utilized in different products. If the CO₂ is converted to a valuable product, the cost of CO₂ capture and utilization may be recovered by the sale of the product. Hence the production cost of electricity can be the same in both cases.

For low carbon transition, the renewable power generation plant installed capacity is increasing rapidly. In future the renewable electricity generation will be high enough that excess electricity will be available in non-peak load conditions. This electricity can be utilized for green hydrogen generation. For base load, there will be requirement of power generation by fossil fuel and the CO₂ in flue gas will be captured. The potential avenues of CO₂ utilization for the product in demand are:

- (i) Basic chemicals like Methanol, Ethanol, Dimethyl Ether, and Methane which can also be used as fuel for energy security.
- (ii) Urea used as fertilizer for food security.
- (iii) Carbon black of different morphologies which is utilized in different important product like in electrodes of rechargeable batteries, production high strength light-weight products, and Different organic chemicals.

The methanol can be used as:

- (i) A fuel, blended with gasoline, or as a raw material to produce biodiesel (dimethyl ether, DME).
- (ii) A raw material for various chemicals, like formaldehyde (mainly phenol, urea, melamine-formaldehyde, polyacetal resins, etc.), methyl tert-butyl ether (MTBE), ethylene and propylene.

The expected annual global methanol production will grow from 100 Mt to more than 120 Mt by end of 2025, and the rate of growth of methanol consumption will be more the 6% per year [3]. Due to this tremendous demand potential of methanol, it seems like a commercially viable option. The model of green methanol generation is based on interlinking 3-Green Pillars together i.e.

- (i) Excess availability of renewable electricity,
- (ii) Electrolysis of green hydrogen, and
- (iii) Carbon capture from the flue gas and its utilization.

The current manuscript describes the 10 TPD capacity demonstration unit of green Methanol synthesis.

2 System Brief

There are three interconnected blocks in the Flue Gas CO₂ to Methanol synthesis (FG-CTM) demonstration plant:

- (i) CO₂ Capture,
- (ii) Hydrogen Generation with Electrolyzer, and
- (iii) Methanol Synthesis by catalytic hydrogenation.

For CO₂ Capture, the flue gas is taken from Flue Gas Desulphurization (FGD) Plant. The Hydrogen Electrolyzer is a Proton Exchange Membrane (PEM) Electrolyzer.

2.1 Carbon Dioxide Capture

CO₂ in the flue gas can be captured in three scenarios:

- (i) Pre-combustion: where the CO₂ is captured after partial oxidation of fuel.
- (ii) Post-combustion: where the CO₂ is captured from the flue gas after complete oxidation.
- (iii) Oxy combustion: where the CO₂ is captured from the flue gas after the complete (or partial) oxidation of fuel in presence of Oxygen instead of air.

A few separation technologies could be employed for CO₂ capture are [4]:

- (i) Adsorption,
- (ii) Physical absorption,
- (iii) Chemical absorption,
- (iv) Cryogenics separation,
- (v) Membranes, and
- (vi) Microalgae.

Most available adsorbents require high CO₂ concentration in flue gas and have low selectivity and detrimental effect of water on typical physisorbents, zeolites. Moreover, large-scale power plant requires large-scale flue gas treatment and present equipment configuration used for adsorption may not be suitable for large-scale applications [5].

Physical absorption of the CO₂ is based on Henry's law. Physical absorption requires high CO₂ partial pressures and gets separated by releasing the pressure. In this process, the main energy is required to pressurize the flue gas. Therefore, for economical CO₂ separation by physical absorption CO₂ partial pressures should be higher than 15 vol%. [6,7].

The CO₂ in the flue gas is liquified and separated from the in cryogenics separation. At atmospheric pressure, CO₂ condenses at -56.6°C . Considering the costs of refrigeration, very high CO₂ concentration and preferably higher flue gas pressure is suitable. Typically, CO₂ is captured by this method after the oxyfuel process.

In membrane separation, the sorption of CO₂ from flue gas to liquid solvent is across the membrane. The membrane absorption devices are more compact than conventional packed absorption columns and are not susceptible to the difficulties in the conventional absorption process. However, to enable sorption of CO₂ across the membrane, the flue gas pressure must be equal to the liquid side pressure. In membrane absorption, the CO₂ separation efficiency depends on the CO₂ partial pressure in flue gas. As such, they are suitable for high flue gas pressure and high CO₂ concentration applications (well above 20 vol%) [8]. The captured CO₂ selectivity and the purity in the membrane separation process is low [6]. Therefore, multistage separation is necessary to improve the CO₂ purity, which requires extra capital and operating cost [6,7].

CO₂ capture efficiency by microalgae ranges between 40% and 93.7% [9]. However, the performance of microalgae in carbon emission reduction has not yet been fully understood and therefore requires more study. In chemical absorption, the solvent forms a weakly bonded CO₂ intermediate compound. Heating this intermediate compound gives the original solvent and a CO₂ stream. Even from gas with low concentration of CO₂, the selectivity is relatively high in chemical absorption, and separated CO₂ is also relatively pure. Therefore, chemical absorption is well suited for CO₂ capture for industrial flue gases.

Almost all thermal power plants in India have pulverized coal boilers, where the flue gas temperature is moderate, around 105–130 °C and CO₂ fraction in flue gas is around 11%–15%. To separate CO₂ from this flue gas, many chemisorption solvents are commercially available. The chemisorption process is exothermic, and the desorption process is endothermic. The temperature requirement for CO₂ desorption is also high (around 110 to 150 °C).

Primary and secondary alkanolamines react rapidly with CO₂ and form the thermally stable CO₂ carbamates with a high heat of absorption. Therefore, the solvent regeneration heat requirement and cost is also high. Moreover, the CO₂ loading capacity of alkanolamines is limited to 0.5 mol of CO₂ per mol of these amines [10]. The tertiary amine bicarbonate formation heat release is lower than that of carbamate formation, thus reducing solvent regeneration costs. Moreover, the CO₂ loading capacity of tertiary amines is 1 mol of CO₂ per mol of amine [10], but the rate of absorption is slow in tertiary amines.

Therefore, the blend of modified amines is used which optimize the rate of fast CO₂ absorption and low temperature & energy requirement for CO₂ desorption. APBS-CDR Max®, KM CDR Process™, BASF PuraTreart™ etc. are few CO₂ capture solvents

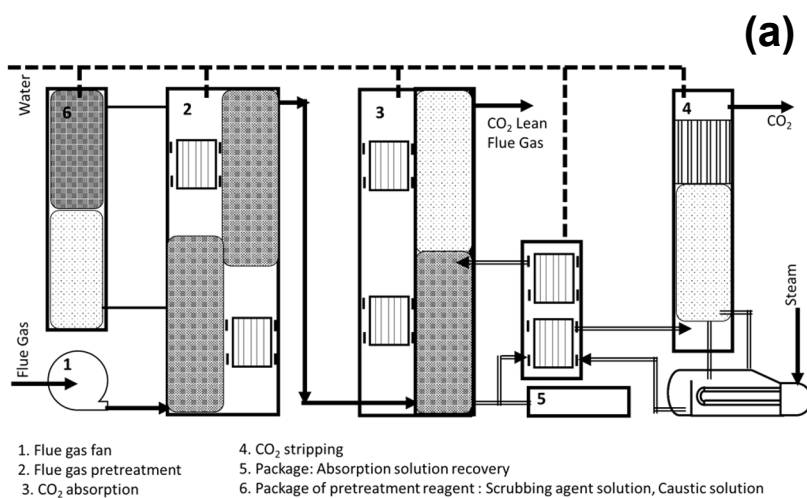


Fig. 1. (a) CO₂ Capture: Process flow diagram **(b)** Photograph of the CO₂ Capture pilot plant at NTPC Vindhyachal.

used in industry for capturing CO₂ from flue gases with CO₂ concentrations ranging from 2.5-25% by volume [4]. The main process in the carbon capture process is that CO₂ is absorbed from flue gas in amine solution, and this CO₂-rich amine solution is stripped by heating. The flue gas contains tiny amounts of particulate matter and sulfur dioxide, which are not removed by the Electrostatic Precipitator (ESP) and flue gas desulfurizer (FGD), respectively. The particulate matter and sulfur dioxide in the flue gas will poison the amine solution. Therefore, the first step before CO₂ absorption is to reduce the flue gas temperature and clean flue gas from particulate matter by water and reduce sulfur dioxide by sodium bicarbonate solution. There is a requirement to remove the heat during the absorption process. There is also a requirement to prevent the amine solution from escaping from the absorber (with CO₂-lean flue gas) and from the stripper (with captured CO₂) as shown in Figure 1(a). To further optimize heat requirements through heat integration, it's important to address impurities in the flue gas, such as sulfur dioxide, nitrogen oxides, and elevated oxygen levels, which can react with amine solvents to form heat-stable salts, leading to solvent degradation. To remove these salts, a portion of the stripper bottoms is directed to a reclaimer unit. In this unit, the solvent is evaporated, allowing non-volatile waste components to be separated. The reclaimed solvent is then returned to the absorber system for reuse. The plant capacity of CO₂ capture plant is 20 TPD and around 14 TPD CO₂ will be used for methanol synthesis. A visual representation of the demonstration plant is provided in Figure 1(b).

2.2 Hydrogen Electrolysis

Hydrogen is produced by breaking down water molecules into Hydrogen and Oxygen by passing them through the electrolyzer. Water is purified by removing traces of impurities/salts and fed into electrolyzer through the anode separator vessel. The following factors are used to compare alkaline and proton exchange membrane (PEM) electrolyzers, illustrating why PEM is often regarded as the superior choice in many applications.

Alkaline electrolyzers have a long operational history and cost-effectiveness. They typically operate at lower current densities (0.2–0.4 A/cm²), which can limit their responsiveness to dynamic power inputs. Since the alkaline electrolyzer has a large liquid electrolyte volume, it is less suitable for applications requiring rapid load changes. PEM electrolyzers employ a solid polymer electrolyte (e.g., Nafion) that conducts protons (H⁺) from the anode to the cathode. PEM electrolyzers offer rapid start-up times and can quickly adjust to fluctuating power inputs, making them ideal for integration with renewable energy sources like wind and solar. Therefore, PEM electrolyzers are used for H₂ generation. [11,12]

To enhance operational flexibility, a PEM electrolyzer has been adopted, capable of functioning efficiently over a wide load range (10–100%) and offering a rapid dynamic response. This makes it more suitable than conventional alkaline electrolyzers for managing variable process demands and aligning with the intermittent nature of renewable energy sources. The PEM allows only protons to pass through while blocking electrons.



Fig. 2. Photograph of the PEM electrolyzer installed at NTPC Vindhyachal.

During operation, the hydrogen atoms in water molecules migrate through the membrane and are released as hydrogen gas on the cathode side. Simultaneously, the remaining oxygen atoms exit from the anode side as oxygen gas along with water. The gas–liquid mixture exiting the anode is separated in the anode separator, while the hydrogen gas on the cathode side, containing trace amounts of water, is processed in the cathode separator.

After this stage, the hydrogen is directed to a dryer unit to achieve the desired purity level. The PEM electrolyzer in use has a hydrogen production capacity of 2 TPD (tons per day), with a discharge pressure of approximately 30 barg. The specific power consumption of the system ranges between 55–60 kWh per kilogram of hydrogen. A photograph of the plant setup is shown in Figure 2.

2.3 Methanol Synthesis Process

The catalytic hydrogenation of CO₂ to methanol presents a promising pathway for mitigating greenhouse gas emissions and producing valuable chemicals. This process typically involves the reaction of CO₂ with hydrogen (H₂) over a catalyst, yielding methanol (CH₃OH) as the primary product. Copper-based catalysts, such as Cu/ZnO/Al₂O₃, have been extensively studied due to their high selectivity and activity for methanol synthesis. Recent developments focus on enhancing these catalysts by doping with elements like ZrO₂, CeO₂, and Ga₂O₃ to improve stability and resistance to deactivation [13,14]. Studies have demonstrated that NiZn intermetallic catalysts, supported on

ZnO, can efficiently catalyze CO₂ hydrogenation to methanol under atmospheric pressure. These catalysts exhibit a high methanol production rate with excellent selectivity, making them promising candidates for solar-driven applications [15]. Photocatalytic reduction of CO₂ to methanol using sunlight has garnered significant attention. Materials such as carbon quantum dots, Bi-based compounds, g-C₃N₄, and metal-organic frameworks (MOFs) have been explored as photocatalysts. These systems aim to harness solar energy for sustainable methanol production [16]. An overview of the literature reviewed is shown in Table 1.

A demonstration plant with a production capacity of 10 TPD Methanol has been integrated with a 500 MW power unit at NTPC Vindhyachal, India, as illustrated in Figure 3. As shown in Figure 4, CO₂ and Hydrogen is compressed in the compression section, the compressed syngas is converted to crude methanol in the methanol synthesis section and the product methanol is purified in the distillation section.

Table 1. Key Studies on CO₂ to Methanol Conversion

Study	Catalytic System	Key Findings
Yusuf & Almomani (2023)	Cu/ZnO/Al ₂ O ₃	Enhanced operating conditions for sustainable catalytic hydrogenation of CO ₂ to methanol [13].
Han et al. (2024)	NiZn/ZnO	High-efficiency sunlight-driven CO ₂ hydrogenation to methanol under atmospheric pressure [15].
Murthy et al. (2021)	Cu-based nanocatalysts	Overview of Cu-based nanocatalyst development for CO ₂ hydrogenation to methanol [14].
Zhang et al. (2021)	Various photocatalysts	Advances in photocatalytic reduction of CO ₂ to methanol using various materials [16].



Fig. 3. Photograph of the 10 TPD Methanol synthesis pilot plant installed at NTPC Vinhyachal.

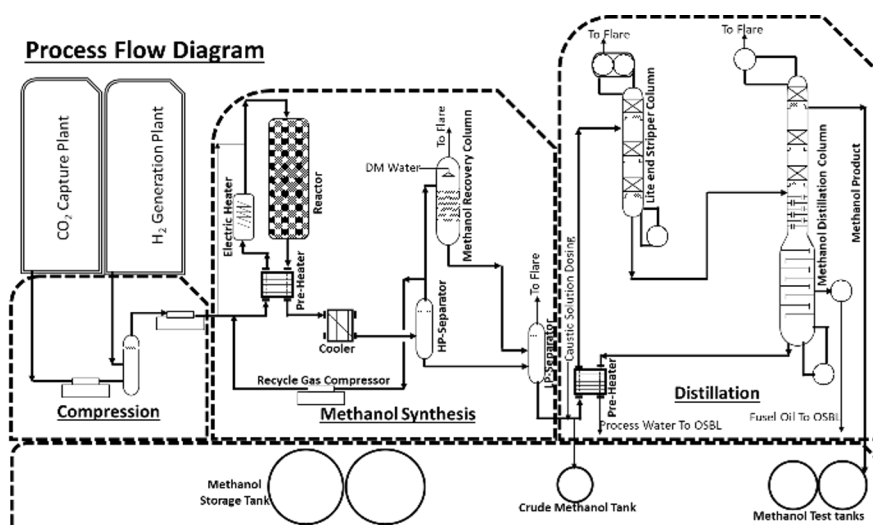


Fig. 4. Schematic of the Methanol synthesis process flow diagram.



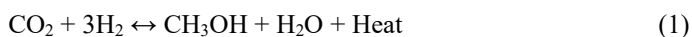
Fig. 5. Photographs of the key equipment installed in the pilot plant. **(a)** CO₂ Compressor, **(b)** Methanol Reactor, and **(c)** Product Methanol Storage Tanks

2.3.1 CO₂ and Syngas Compression

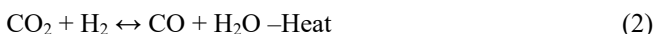
The CO₂ gas is initially compressed to 30.0 barg in a CO₂ compressor as shown in Figure 5(A). The H₂ gas is then mixed with the compressed CO₂, and now the mixture is called syn gas. The syngas, which is now at 30 barg is further compressed to 60 barg in the Synthesis Gas Compressor. The syngas temperature is raised to 235 °C -250 °C in the Electric heater.

2.3.2 Methanol Synthesis Reactor

Preheated syngas (Temperature around 235 °C - 250 °C) is now fed in the Methanol Reactor as shown in Figure 5(B). The Methanol Reactor contains a fixed bed of Cu catalyst to convert carbon dioxide and hydrogen to methanol and water.



The synthesis of methanol from CO₂ (Equation (1)) is less exothermic as compared to starting from CO in syngas, and it also involves a secondary reaction in the reverse water–gas shift (RWGS) (Equation (2))



The methanol synthesis process mostly uses Cu/ZnO/Al₂O₃ catalyst which can ensure appreciable performance at low temperatures. Some commercially available catalysts are MK-151 FENCE™ by TOPSOE, KATALCO™ 51-series by JOHNSON MATTHEY, MEGAMAX® 800 by CLARIANT, etc. The reactor outlet contains about 2.8 mol% methanol and the temperature is around 260 °C - 290 °C. The reactor outlet is first cooled in Synthesis Gas Heat Exchanger, which in turn preheats the feed of Methanol Reactor. To separate crude methanol, Methanol Reactor outlet is then further cooled to 40 °C and flashed in the HP Separator to separate out the unreacted gas and crude methanol liquid. Part of the unreacted gas from HP Separator is purged to maintain the inert gas level in the Methanol Reactor feed. Before purging the gas to flare, methanol is recovered in the Methanol Recovery Column. The remaining part of the unreacted gas from HP Separator is recycled and mixed with fresh make-up gas to pre-heat and to feed to the methanol reactor. There is an Electric Heater downstream of the preheater of the reactor. The Electric Heater is used for process start-up and for heating low-temperature reactor feed to maintain the temperature. To permit adequate control on higher reactor feed temperature, the feed syngas bypass is also provided around both exchangers.

2.3.3 HP Separator/ LP Separator/ Methanol Recovery Column

Crude Methanol collected in HP Separator and in Methanol Recovery Column is sent to LP Separator. The LP Separator separates the dissolved gases such as CO, H₂ and CO₂ from the crude methanol. The gases coming from LP Separator and Methanol Recovery Column go to flare. Crude Methanol collected in LP Separator is sent to the distillation section. There is also a provision to store crude methanol in Crude Methanol Tank along with the Product Methanol Test Tank and Product Methanol Storage Tank as shown in Figure 5(c).

2.3.4 Methanol Distillation

Crude methanol from the Methanol Synthesis Section is sent to the Distillation section for methanol purification. The distillation is carried out in two steps,

- (i) Light End Stripper
- (ii) Methanol Distillation column

Light End Stripper

Light End Stripper removes the dissolved gases like CO, H₂, CO₂, together with other light ends formed during the methanol synthesis reaction, such as dimethyl ether and

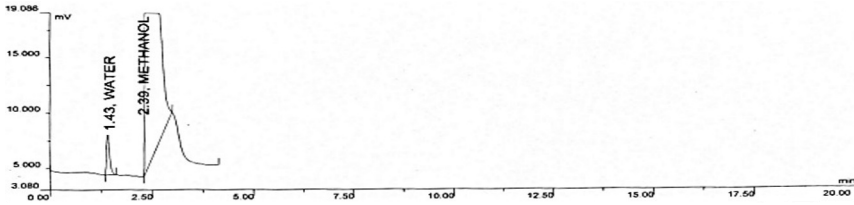


Fig 6. FID - GC plot showing the peak intensities obtained for the methanol sample obtained from the stripper reflux drum section.

methyl formate. The condensed methanol is fed back to the top of the light-end stripper column. The light end stripping column is operated at 0.4 barg pressure with a bottom temperature of 89 °C and a top temperature of 72 °C.

Methanol Distillation column

The purpose of Methanol Distillation column is to remove water and organic heavy ends and thus purify the methanol product. The heavy ends are predominantly alcohols such as iso-butanol and are known as fusel oil and water. The product methanol is withdrawn from top section of the column, cooled to 40°C, and sent to the Product Methanol Test Tank. Then, the product methanol is delivered to the Product Methanol Storage Tank. The Methanol distillation column is operated at 0.5 barg pressure with a bottom temperature of 125 °C and a top temperature of 75 °C. Fusel oil, is drawn off at an intermediate bed located in the stripping section of the column. The processed water collected from the bottom of the column is cooled through the Crude Methanol Heater. The methanol plant capacity is 10 TPD and utility consumption for all individual plants is given in Table 2.

The methanol sample was obtained through a sampling line at Stripper Reflux Drum. The methanol sample was analyzed for purity through gas chromatography (GC) technique equipped with a flame ionization detector. Figure 6 shows the FID - GC plot, it can be clearly seen that the methanol purity was 99.85% and the remaining was water; conforming to ASTM D – 1152 standard.

Table 2. Utility consumption in different blocks

No	Utility	Units	CO ₂ Capture	H ₂ Generation	Methanol Synthesis
1	Steam	kg /hr	1,600	-	982
2	DM water	kg /hr	120	1,000	1,500
3	Service water	kg /hr	600	-	13,000
4	Power	MW	0.2	5	1

3 Conclusion

The present manuscript has presented the conceptualization, design, and implementation of a carbon dioxide-to-methanol synthesis facility. The 10 TPD methanol demonstration plant represents a pivotal milestone in assessing the technical and economic viability of mitigating greenhouse gas emissions associated with coal-fired power generation. The facility is expected to yield critical operational data that will inform the techno-economic analysis necessary for scaling to a commercially viable, full-scale production system. The facility was able to produce 99.85% purity methanol which was confirmed through FID – GC technique.

This initiative aligns with the strategic objectives of NTPC Ltd., and the broader Indian power sector to substantially reduce carbon emissions in line with the CoP 26 agreements and commitments. It also contributes to the realization of India's Methanol Economy framework and the national Net Zero emissions target by 2070. By maintaining a systems-level integration across all stages of the process, the project enhances its translational relevance for industrial stakeholders and the scientific research community.

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