

Methanol Emission from Ammonia Plants and its Reduction

The CO₂ that is removed from the synthesis gas in an ammonia plant is released to the ambient air if it is not used by another process. This CO₂ stream can contain a considerable amount of methanol.

Methanol, like other volatile organic compounds (VOC), contributes to the formation of photochemical smog which consists mostly of ozone (O₃). Since ozone adversely affects human health, limits are set in many parts of the world. Consequently, in many places (e.g. the USA) limits have been placed on the emissions of its precursors.

These limits become a challenge for ammonia producers. Methanol is generated as an unwanted by-product in the CO shift reactors. Part of it is removed from the process gas with the process condensate. The remainder passes to the CO₂ removal unit and ends up in the CO₂ stream.

This paper briefly describes the effect of methanol in the atmosphere and the process by which methanol is formed in an ammonia plant. It focuses on ways to reduce emissions by reducing the amount that is formed, by process changes and by “end of pipe” abatement.

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Introduction

Terms like summer smog and ground-level ozone are well known to many of us because they impact our daily life. Many of us, for example, know the appeals to avoid outdoor physical efforts under certain climatic conditions in the summer.

Summer smog (also called photochemical smog, ozone smog or Los Angeles smog) arises from the pollution of ground-level air by high concentrations of ozone. It occurs during sunny

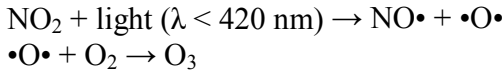
weather and is created from nitrous oxides and hydrocarbons in presence of ultraviolet (UV) radiation. It attacks respiratory organs and harms animals and plants.

Effect of Methanol Emissions on the Atmosphere

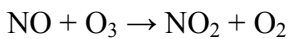
Ozone Formation

Ground-level ozone is formed from nitrous oxides under the influence of the ultraviolet (UV) radiation of the sun. Nitrogen dioxide (NO₂), emitted by combustion processes into the at-

mosphere, is split by UV radiation into nitrogen monoxide (NO) and an oxygen atom. This atomic oxygen combines with an oxygen molecule, forming ozone (O₃):

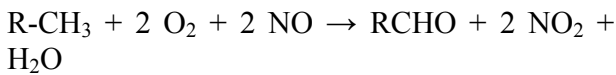


At the same time, nitrogen monoxide (NO) decomposes ozone to form nitrogen dioxide and oxygen:



As ozone is simultaneously being formed and being decomposed, an equilibrium concentration can be defined. During the night (no UV radiation), decomposition dominates and the ozone concentration falls.

Ozone formation is favored by volatile organic compounds (VOC, R-CH₃) because they help to form nitrogen dioxide from nitrogen monoxide in the presence of sunlight:



The reaction mechanism is summarized in a simplified form in Figure 1.

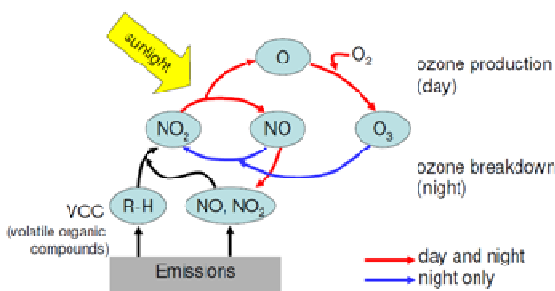


Figure 1. Ozone formation mechanism (simplified from [1])

In order to quantify ozone formation potential, the MIR (maximum incremental reactivity) scale has been developed, and values have been determined for many hydrocarbons (Table 1).

This scale has been developed to characterize the potential for ozone formation under certain atmospheric conditions by the components present in the exhaust gases of internal combustion engines.

Substance	MIR
Olefins	8 to 11 g O ₃ / g VOC
Aromatics	7 to 9 g O ₃ / g VOC
Methane	0.015 g O ₃ / g VOC
Methanol	0.67 g O ₃ / g VOC
Methyl diethanolamine (MDEA)	no value available

Table 1. MIR Values for several substances [2]

Effects of Ozone on Humans

Ozone enters the lungs and can cause inflammation. Depending on the time of exposure and on physical exertion the effects can be coughing, irritation of the eyes, headache, and functional disturbance of the lungs. Therefore, physical exercise should be avoided when ozone levels are high.

Regulatory Limits

Due to the adverse effects of ozone, regulatory limits have been imposed. For example, within the European Union [3] the limits are as follows:

- Maximum daily concentration (8 h average) target value of 120 µg/m³
- Information to the public when 1 h average concentration > 180 µg/m³
- Warning to the public when 1 h average concentration > 240 µg/m³

For the USA, EPA has set the National Ambient Air Quality Standard (NAAQS) for ozone to 0.075 ppm (8 h average) (equivalent to 160 µg/m³) [4].

For comparison, the normal concentration of ozone in the ground-level atmosphere is 40 to 80 µg/m³ (≈0.02 to 0.04 ppm).

Countermeasures

When thinking about countermeasures against high ozone concentration, the following must be considered:

- ozone cannot be attributed to a single point of emission because it is formed within the atmosphere, and
- the weather as one of the originators cannot be changed.

As a result, measures are taken to limit the emissions of its precursor substances; NO_x and VOC from industry, traffic and households.

Short-term measures to limit ozone include shutting down industry and limiting traffic when ozone levels are high. Longer-term measures involve modifications to facilities and vehicles, some of which are already being implemented. For example, on large furnaces, (catalytic) NO_x removal is standard in many countries; for vehicles, the contribution to ozone formation has been reduced by exhaust gas catalysts by 80 to 95%, reducing NO_x, CO and VOC emissions.

In the USA, New Source Review (NSR) threshold for significant emissions increase of VOC and NO_x for ozone regulation is 40 tons per year [5]. Methanol is classified as a Hazardous Air Pollutant (HAP). A release of more than 10 tons per year is considered a “major source” and is controlled by the EPA [6].

Methanol Emissions from Ammonia Plants

Methanol Formation

Figure 2 illustrates the parts of an ammonia plant which are relevant to the formation of methanol and its path through the process to the points of emission. It also serves as the base for the discussion of reduction of ammonia emissions discussed later in this text.

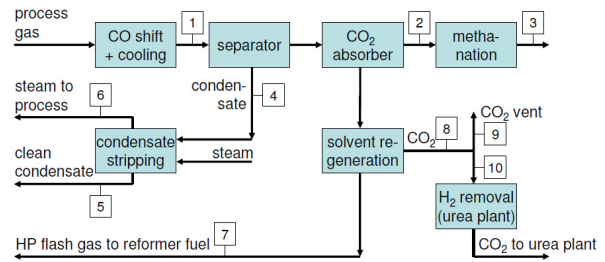
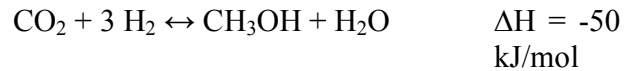


Figure 2. Simplified flowsheet of CO shift, CO₂ removal, and condensate stripper of an ammonia plant

By-products are formed, in small quantities, across both HTS and LTS catalysts. Of these the largest component by far is methanol, which is believed to be formed by the reaction of carbon dioxide with hydrogen ([7]).



The chrome phase is believed to promote methanol formation across HTS catalysts (not surprising as early methanol catalysts were chrome based). The presence of copper also contributes.

As copper is the active component in both methanol synthesis and LTS catalysts, it is not surprising that LTS catalyst will, to an extent, catalyze the formation of methanol.

Whilst the methanol concentration leaving the HTS catalyst is close to equilibrium and therefore independent of catalyst type, methanol formation in LTS catalysts is kinetically limited and does not usually reach equilibrium. As the methanol forming reaction is exothermic, and HTS catalysts operate at higher temperature, the shape of the equilibrium curve dictates that methanol formation across HTS catalysts is substantially less than that across traditional, non-selective LTS catalysts (Figure 3).

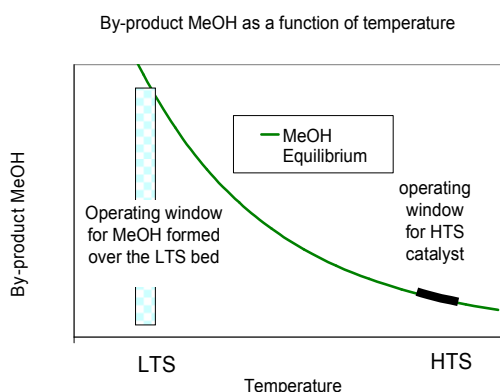


Figure 3. Effect of equilibrium on methanol formation

LTS catalyst is slightly unusual in that selectivity increases, and by-product formation decreases, as the catalyst ages (Figure 4). This behaviour is because the activity with regard to methanol synthesis declines as the active sites for methanol synthesis decrease. There is no corresponding impact on the activity with regard to the shift reaction, which, in a well-structured catalyst, remains high enough to maintain an equilibrium CO slip.

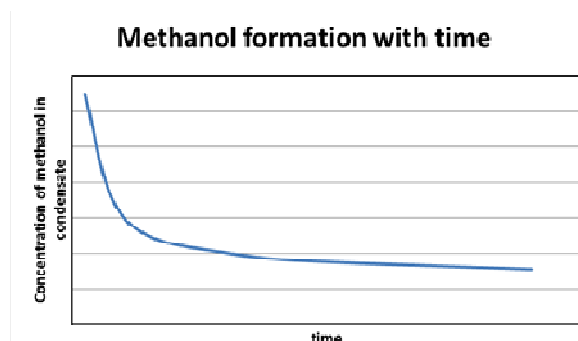


Figure 4. Methanol formation with time across an LTS catalyst

Process Condensate Treatment

The gas leaving the LTS is cooled and condensate is removed via the process condensate separator. The split of methanol is determined by vapor-liquid equilibrium, hence the lower the temperature, the greater the proportion of methanol that is removed via the process condensate, as illustrated in Figure 5.

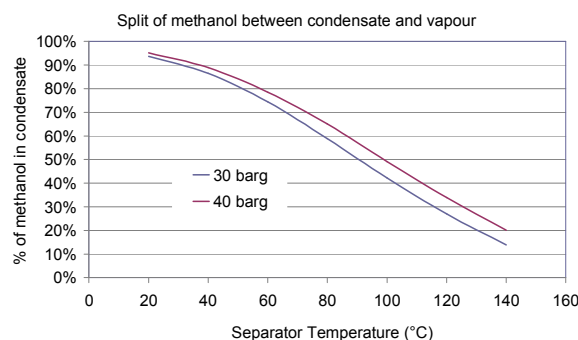


Figure 5. Split of methanol between condensate and vapor for a modern ammonia plant

Modern plants, and older plants retrofitted with condensate strippers in the last couple of decades, use a medium pressure stripper to treat the condensate. A well designed stripper meets most environmental standards for waste water and will recycle methanol to the reformer feed.

Plants with older designs of stripper can use LP stripping to remove methanol and ammonia from the condensate. Sometimes they are vented to atmosphere along with the stripping steam, but more commonly the vent stream is condensed and sent, for example, to a feed coil saturator (although sometimes a small, methanol containing stream is “purged” to atmosphere).

Methanol Remaining in Process Gas

The methanol that is not removed in the process condensate separator passes into the CO₂ removal system. The majority of that CO₂ passes into the saturated CO₂ product, with its fate intertwined with that of the CO₂ product. The few parts per million that remain in the treated syngas (stream no. 2 in Figure 2) decompose in the methanator.

The methanol absorbed by the CO₂ removal solution in the absorber is almost completely expelled from it in the regeneration section. In Figure 2, which represents a plant with an activated MDEA CO₂ removal unit, the CO₂ containing streams are the high-pressure flash gas

(stream no. 7) and the high-purity CO₂ stream (stream no. 8). The HP flash gas stream is normally used as reformer fuel, and the methanol and other hydrocarbons contained within it are combusted and do not appear as an emission. In a typical system, about 8% of the methanol leaves with the HP flash gas and about 92% leaves with the CO₂ stream.

If the CO₂ is scrubbed, cooled or compressed, a methanol containing liquid effluent can be created. In many plants, the volumetric flow is small enough for this either to be disregarded, or to be treated by pumping it into the process condensate stream for purification in the existing process condensate stripper.

Compression and cooling is the case when part, or all, of the CO₂ stream is used in a urea plant (stream no. 10). Methanol and water condense and are separated from the gas in the inter-stage separators of the CO₂ compressor. The remaining CO₂ is removed in the H₂ removal reactor by catalytic conversion with O₂.

A methanol containing gaseous effluent stream can be created if CO₂ gas is vented, or, as happens on some food grade CO₂ plants, it passes through a solid adsorbent which is then regenerated.

Methanol Emission Reduction

Overview

Several options exist for reducing methanol emissions including the following:

- Reducing the amount that is formed.
- Removal or decomposition of the methanol within the process.
- Removal or decomposition at the point of emission.
- Combination of the above schemes.

Reduction of Methanol Formation

The amount of by-product methanol produced in the LTS converter is influenced by a variety of factors, which are summarized in Table 2. In most plants, there is only limited flexibility to change operating conditions with the result that LTS catalyst selection is the only real alternative for reducing methanol by-product formation. Selective low methanol LTS catalysts such as **KATALCO_{JM} 83-3X**, reduce methanol formation by about 90% compared to conventional non-selective LTS catalysts. As the relative contribution to methanol formation from the LTS falls, that from the HTS increases, and methanol emissions can be grossly underestimated if formation across a selective LTS is considered in isolation (Figure 6).

Increase in	Effect on methanol make
Steam / H ₂ ratio	↓
Inlet temperature	↑ (if not at equilibrium) ↓ (if at equilibrium)
Pressure	↑
Space velocity	↓
Catalyst age	↓
Catalyst selectivity	↓

Table 2. Effect of various operating parameters on methanol production

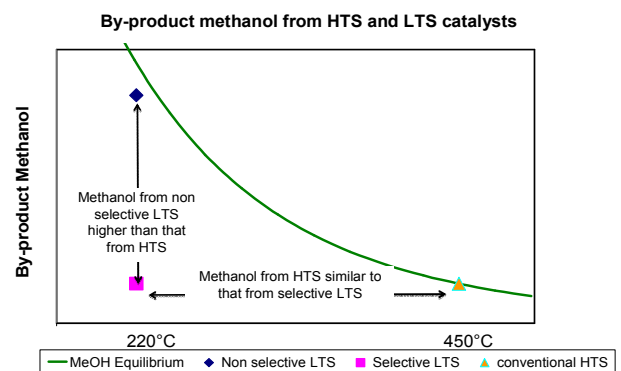


Figure 6. By-product methanol from LTS and HTS catalysts

It is critical therefore that a catalyst supplier is able to provide an accurate prediction of the level of methanol that both HTS and LTS catalysts will make during their service life. Johnson Matthey uses models developed with the Technical University of Delft to enable detailed and accurate predictions of by-product methanol levels to be made [7].

Reduction of Emission by Process Measures

As illustrated by Figure 5, on most plants, less than half of the methanol will enter the CO₂ removal unit, and the proportion falls as the separator temperature is lowered. A typical inlet temperature to an absorber on an amine system is 70 to 75 °C (160 to 170 °F). A lower temperature is possible but may require a slightly taller absorber or more effective packing due to the reduction in the rate of absorption of CO₂ at lower temperatures.

A temperature reduction to approximately 50 °C (120 °F) is possible with little effort because it can be reached by cooling the process gas with cooling water or demineralized water. To achieve lower temperatures chilling is required. Both investment and operating cost increase if the gas is cooled or chilled (e.g. by a chiller connected to the refrigeration unit of the plant), even when part of the cooling duty is provided by heat exchange with the gas for re-heating it again to the necessary inlet temperature of the absorber. Cooling the gas fed to the CO₂ absorber has only little impact on the rest of the process, the only material change being an increase in the load placed on the condensate stripper.

With a two-cycle activated MDEA system, it is hardly possible to influence the methanol balance by process variations:

- A reduction in the HP flash pressure leads to only marginal reduction in methanol concentration in the CO₂ vent.

- Increasing the number of back wash trays at the absorber top increases the methanol concentration in the CO₂ vent.
- Increasing in the number of back wash trays in the LP flash does not reduce the concentration of methanol in the CO₂ vent.

With a CO₂ removal system based on hot potassium carbonate, the inlet temperature is about 90 °C (190 °F). There is less flexibility to reduce the inlet temperature, as the solution tends to crystallize at low temperatures and it is normally recommended that the loaded solution (absorber bottom) should not fall below 70 °C (160 °F).

Table 3 shows the typical distribution of the methanol through the ammonia process.

Separator temperature*	Stripped condensate	Steam to process	HP flash to fuel	vent or urea plant
	stream 5	stream 6	stream 7	stream 8
10 °C (50 °F)	2.2%	94.1%	0.2%	3.4%
30 °C (85 °F)	2.1%	89.2%	0.6%	8.0%
50 °C (120 °F)	2.1%	80.2%	1.2%	16.3%
75 °C (165 °F)	2.1%	63.6%	2.3%	31.7%

*) separator upstream of CO₂ absorber

Table 3. Distribution of methanol through the process in percent of methanol present downstream of LT shift. Stream numbers refer to Figure 2

Streams 6 and 7 lead to decomposition within the process. Only stream 8 leads to a potential gaseous emission.

Reduction by Removal at the Point of Emission

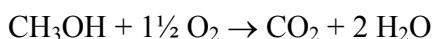
Methanol emissions can also be reduced by modifying the CO₂ removal system with the in-

tent that more methanol is trapped in the condensate downstream of the CO₂ coolers (stream 8 in Figure 2). To lower the methanol equilibrium concentration in the gas phase, the liquid phase must also have a low methanol concentration. This means that some of the methanol-containing condensate has to be removed from the process and replaced with pure water. The bleed stream of methanol-containing condensate can be sent to a stripper in order to avoid enrichment of the methanol in the condensate. The bleed flow must be fairly large even for a small reduction in methanol emissions. On the other hand, the condensate contains traces of the amine employed in the CO₂ removal. To avoid the loss of the amine one would prefer to return as much as possible the condensate to the CO₂ removal process.

At the usual low pressure in the regeneration section methanol tends to stay in the vapour phase so that the lowest level that can be achieved is around 80 ppmv. Using chilled water for regenerator overhead cooling to 10 °C (50 °F), instead of 50 °C (120 °F), reduces this concentration by only 20 ppmv.

Removal of Methanol by Catalytic Oxidation

To achieve very low emission levels in the range of a few ppm, methanol must be removed from the CO₂ vent stream. Gaseous streams can be treated by catalytic oxidation using technology for VOC removal, which has already been proven in other industries. Catalytic oxidation requires a slight excess of oxygen over the quantity required by stoichiometry. This excess can conveniently be achieved by injecting air into the CO₂.



Monolithic catalysts coated with a very thin layer of platinum or palladium are used on vent streams so as to minimize pressure drop (Figure 7). When the CO₂ is at pressure, catalyst pellets are often more economic.

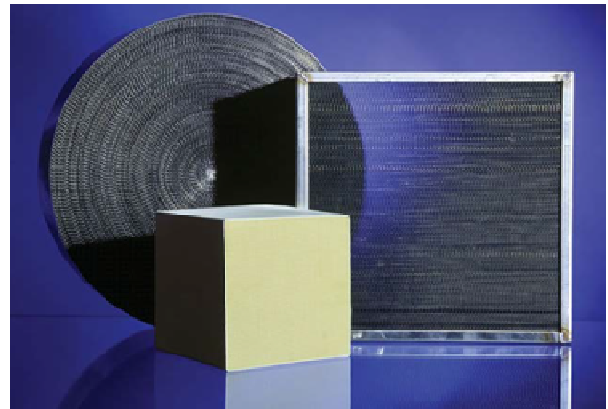


Figure 7. Catalysts for VOC reduction

Although the technology is similar to that used for hydrogen removal on the CO₂ feed to urea plants, higher temperatures are necessary (Figure 8). Since venting usually takes place upstream of any compression, heat of compression cannot be used as a source of heat. The heat therefore has either to be provided externally or by internal combustion (eg: in a recuperative system).

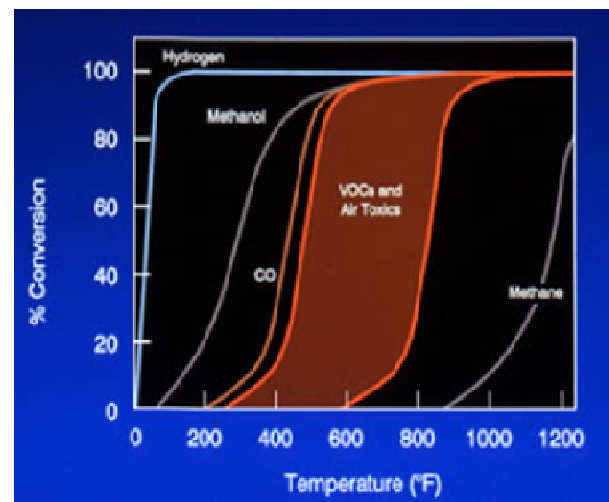


Figure 8. VOC conversion as a function of temperature

Economic Considerations on Methanol Emissions

Besides environmental aspects, there is also an economic driver to reduce methanol formation

by the process, at least to the extent that additional costs are not prohibitive. Methanol formation in the CO shift consumes hydrogen which would otherwise be used to make ammonia. In broad terms, every tonne of methanol that is formed (and not recovered to the reformer feed via the process condensate stripper) results in a loss of 1.1 tonne of ammonia. This loss in its own right can be a powerful incentive for installing a selective LTS catalyst such as **KATALCO_{JM} 83-3X**.

In addition, methanol is an oxygen containing component which must be removed from the process gas before it is fed to the ammonia synthesis. This removal is normally achieved in the methanation by reaction with hydrogen.

Stripping of process condensate is a very economical way to reduce the methanol content in the process condensate to make it ready for reuse as make-up water to the demineralization unit, thus reducing raw water consumption.

Size of the Methanol Reduction Systems

If the ammonia plant is coupled to an adjacent urea plant, the majority of the methanol containing CO₂ stream is used as feed to the urea plant. In such a situation it does not lead to emissions during normal operation of the complex.

If the authorities allow emissions for the limited amount of time of the year whilst the urea plant is not in operation, an “end-of-pipe” methanol reduction system as described above might be designed only for the quantity of CO₂ vented during normal operation. This allowance can lead to a significant cost advantage when compared to the systems described above which are fully integrated into the ammonia process and which ensure a low methanol concentration for the full amount of CO₂. In this case they have to be designed for the full flowrate of process gas, with no reduction in size being possible.

The economics of a process which absorbs the methanol from the CO₂ stream downstream the regenerator in the CO₂ removal unit, depends on the following decisions: For a simple system, there is just a bleed stream and a make-up by fresh water. Possibly, the CO₂ of stream 8 is cooled below ambient temperature to condense as much liquid as possible. A more complex system would contain an additional absorber installed in stream no. 9 and a desorption for example by sending the water to the already existing condensate stripper.

If an “end-of-pipe” system has to be designed for the maximum possible amount of CO₂ vented, it will need to operate at 5 to 6% of capacity most of the time (basis: 2,200 MTPD ammonia plant with a 3,500 MTPD urea plant) and will experience 100% load only a few times per year.

The favored option might be different for a new project than a retrofit. In the first case, one is free to design the plant right from the beginning for low emission figures. In the latter case, it can be difficult to accommodate changes in process temperatures due to limitations in space for additional equipment or availability of utilities.

Comparison of Operating Costs

Emission reductions inevitably require additional investment and lead to increased energy consumption. With the exception of the benefits that can be obtained through the use of selective LTS catalysts, there is little economic incentive to reduce methanol emissions. None of the removal or abatement systems convert the methanol into a valuable product, but all of them consume energy, as highlighted in Table 4.

Lower temperature at condensate separator (cooling with CW)	More condensate to be stripped.
	More cooling water needed
Lower temperature at condensate separator (cooling with chillers)	More condensate to be stripped.
	More cooling water needed
	Chilling duty is needed (electric power / steam)
Catalytic methanol removal at vent	Methanol is combusted and CO ₂ is formed by this process.
	Air blower needed (electric power)

Table 4. Energy consumption implications of methanol removal

Summary and Conclusion

As with other VOC emissions, methanol emissions from ammonia plants are considered to contribute to ground-level ozone. Consequently, in many places of the world, targets and regulations exist to reduce VOC emissions. Regulators are starting to pay more attention to VOC emissions on ammonia plants and this trend is likely to increase.

Several technical options exist to reduce these emissions, including the following:

- Reducing methanol by-product formation in the LTS catalyst.
- Modifying the CO₂ removal process.
- End-of-pipe solution.

Lowest VOC emissions can be achieved only by catalytic conversion at the point of emission. However, by combining it with the other options, the amount of methanol to be converted in the emission stream can be reduced.

Since the VOC emissions are influenced by several process parameters and catalyst properties,

one should not prematurely decide on one technical solution. It is recommended to look at the process in close co-operation with the catalyst vendor, CO₂ removal licensor, and overall process licensor and contractor, in order to obtain the best overall solution.

References

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