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Technology Readiness Level Assessment of Formalin Production Pathways

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Formalin is among the highest production volume chemicals and can be obtained by several production pathways, though there are several potential production pathways in earlier development stages. To evaluate the maturity level of formalin production technologies, assessment is performed according to Technology Readiness Levels (TRL). TRL is a method used to describe the maturity of technologies, and assign them a TRL level or a range of levels from 1 to 9, with TRL 9 indicating the most mature technologic systems. Formalin is most synthesized from methanol produced via syngas which is obtained by steam reforming of natural gas. Other production pathways are formalin produced from biogas, through gasification of biomass, coal, black liquor and other, through methanol produced by direct hydrogenation of CO_2 or via reverse water gas shift reaction, also known as the CAMERE process. Finally, emerging technologies such as direct conversion of methane, syngas or CO_2 to formalin were considered. This work will contribute to a wider understanding of the various technologies used in the formalin production field.

1. Introduction

Formaldehyde is a widely produced bulk chemical (Talaiekhozani et al., 2013) and an essential building block for a variety of chemical products (Subasi, 2020) mainly due to its high reactivity and versatility (Koivikko et al., 2011). Formalin is around 37 wt.% aqueous solution of formaldehyde and is the most common formaldehyde product (PubChem, 2019). Formalin is mostly produced by subsequent processes of steam reforming of natural gas, methanol synthesis, and formaldehyde synthesis from methanol and air. This natural gas reforming pathway accounts for more than 90 % of the formaldehyde production in the world (Bertau et al., 2014). However, there are several other raw materials that could be used as substitutes for natural gas, such as coal, biomass, and other carbon-based sources.

Methanol, which is a precursor to formalin, can also be produced by different pathways. There has been an increase in research of alternative technologies of methanol production such as hydrogenation of CO_2 to produce methanol. This technology has reached a high enough level of readiness to be implemented at the industrial level (Álvarez et al., 2017). Additionally, there are promising technologies in the research stage where methanol could be produced by means such as photocatalytic reduction, as well as technologies for the direct synthesis of formalin from CO_2 or methane. Despite these advancements, however, there has been a lack of comparison between current industrial practice and technically competitive processes which offer potential improvements from an economic and environmental perspective.

A key tool for identifying the perspectives of a new technology is the technology readiness level (TRL) assessment. TRL enables a standardized assessment of the maturity of a particular technology and the consistent comparison of the maturity between different types of technology (Frerking and Beauchamp, 2016). Technology readiness measures the extent to which a technology is suited for deployment in a real operational environment. It is also often used as a measure of risk or uncertainty associated with introducing new technologies. Technology readiness research examines the evolution of a technology from exploratory studies to laboratory experiments, real operational demonstration, and eventually full integration, by dividing the development process into specific TRLs with requisite indicators (Engel et al., 2012). As technologies are evaluated, they are assigned a TRL or a range of levels from 1 to 9 using various available standardized frameworks, with TRL 9 indicating proven and operating technologic systems. It should be noted that since TRL

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assessment measures complex technological cases, the use of its definitions can be subjective and challenging to apply consistently (Beims et al., 2019).
The novelty of this study is its investigation of the readiness levels of chemicals production technologies, specifically regarding formalin production. There is currently a lack of research related to assessing the current state of technologies for production of such bulk chemicals. The objective of this paper is to provide an overview of the different formalin synthesis routes and to use the TRL assessment in order evaluate the readiness level of technologies used in the production pathways. As implementation of new formalin production technologies presents challenges such as low product conversion and selectivity, gaining an understanding of the current technological status presents an important development in the chemical industry. To perform a comparative assessment, formalin production technologies described in research studies were classified into a TRL scale according to level definitions and indicators found in literature.

2. Production pathways

In this section, the formalin production pathways are presented and sorted in different groups: (1) Formalin synthesis via conversion of syngas, (2) Alternative routes via methanol from CO_2, (3) Direct conversion to formalin. The technologies studied in this work are presented in Figure 1.

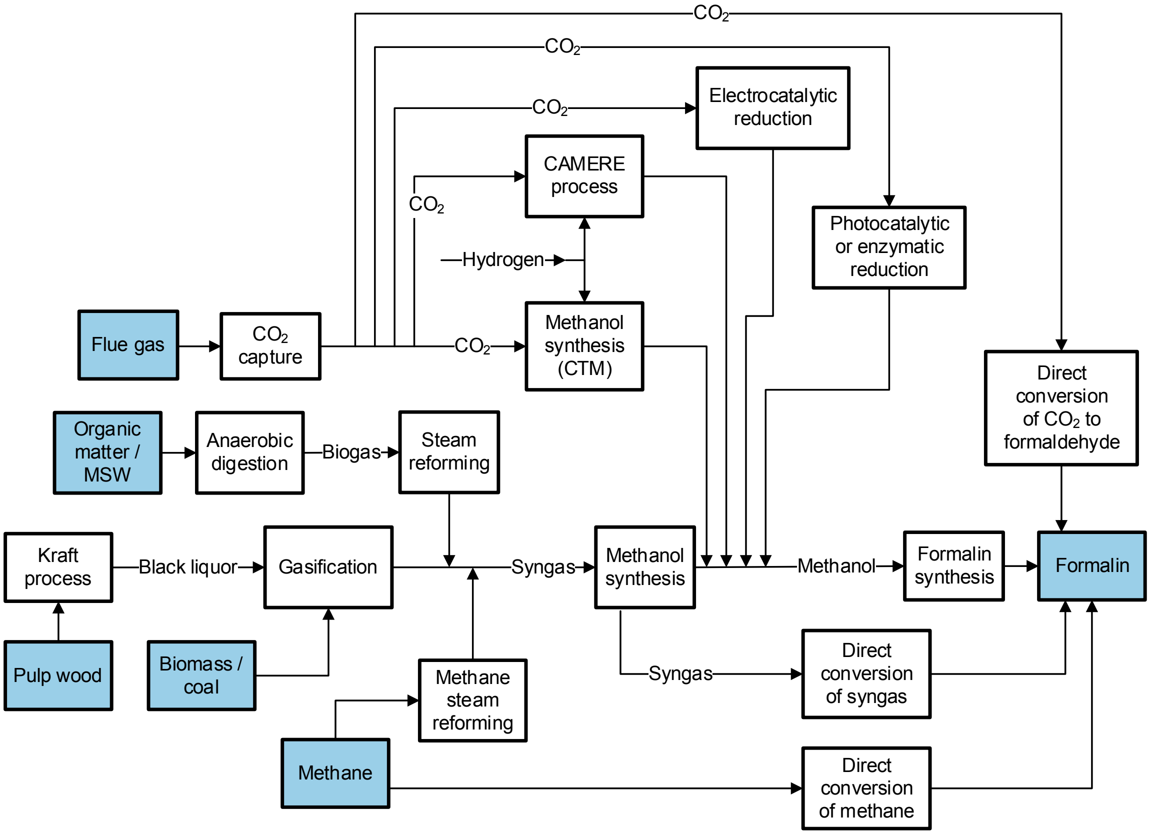

Figure 1: Formalin production pathways

2.1 Formalin synthesis via conversion of syngas

Synthesis gas or syngas is a fuel gas mixture comprised mainly of H_2 and CO and is produced from coal, biomass or any other hydrocarbon feedstock. Syngas conversion is the most common industrial pathway for formalin production. During the process, syngas is pressurized and converted to crude methanol over a catalyst, which is then distilled to remove water and yield pure methanol. Formaldehyde is further synthesized from methanol and air, where the most common commercial process today uses the presence of a silver oxide catalyst in a fixed catalytic bed reactor (Millar et al., 1995). The syngas used in the process can be obtained via different pathways and feedstocks:

- Formalin from natural gas is currently used to produce most of the formalin in the world. The process, which has been simulated and described in previous work (Puhar et al., 2021), is comprised of three main steps:

(1) consecutive reactions of methane steam reforming (MSR) and water-gas shift (WGS) to produce syngas, (2) methanol synthesis and (3) formalin synthesis.

- Syngas may be produced via gasification of various bio-based sources, such as coal or biomass. The process is comprised of three main steps: (1) feedstock preparation, (2) gasification to produce raw syngas, and (3) syngas purification. Methanol and formalin are further produced from syngas like in the natural gas-based pathway.
- Syngas is also produced from black liquor, a by-product of the Kraft process (Di Francesco et al., 2021), where wood is digested into pulpwood. Black liquor is a significant source of biomass and offers advantages for the gasification process, such as its liquefied form and a low methane content in the syngas (IEA Bioenergy, 2007).
- Another promising alternative to produce syngas is biogas from materials such as manure, plant material or municipal waste. Biogas, a mixture of mainly CH_4 and CO_2, is obtained via anaerobic digestion. Syngas is then obtained from biogas via MSR, which is the preferred method due to the presence of steam, which favors the WGS reaction and increases the H_2 content in the resulting syngas (Vita et al., 2018).

2.2 Alternative routes for methanol synthesis

The hydrogenation of CO_2 to produce methanol may be an environmentally viable alternative to the traditional syngas route. The technologies described in this section employ CO_2 captured from flue gases by means of chemical or physical absorption. The following technologies are considered:

- Formalin produced via methanol from CO_2 capture, also known as CO_2-to-methanol (CTM). This technology considers renewable sources, as methanol is produced by catalytic hydrogenation of CO_2, where hydrogen is produced via electrolysis of water (Meunier et al., 2020). Methanol and compressed air are later used to produce formalin.
- CAMERE process for conversion of CO_2 to methanol, an alternative to the CTM technology. In this process, part of the CO_2 is first converted to CO via a reverse WGS reaction (RWGS), which allows for removal of water and reduces water content in the resulting methanol solution (Aničić et al., 2014).
- Electrocatalytic reduction of CO_2 to methanol, where syngas is formed from CO_2 via electrolysis and is used to produce methanol by the process described in Section 2.1. The electrolysis method utilizes a solid oxide electrolysis cell (SOEC) and material inputs of water and flue gas, from which CO_2 is captured. Inside the SOEC, the reactions of water electrolysis, CO_2 electrolysis and WGS are all occurring, resulting in syngas produced from CO_2 and water, where the amount of H_2 is increased because of the WGS reaction (Al-Kalbani et al., 2016).
- Reduction of CO_2 to methanol by other means, such as photocatalytic or enzymatic reduction. The photocatalytic method can produce methanol via reduction of CO_2 with water in the presence of light irradiation (Ali et al., 2015). The enzymatic process utilizes various enzymes to produce methanol from CH_4 and CO_2 which act as sources of carbon. This is a useful method when using biogas, where CH_4 and CO_2 exist in mixture with H_2 (Patel et al., 2016).

2.3 Direct conversion to formalin

There are several technologies in the research stage where formalin could be obtained by direct conversion from precursors such as CO_2, syngas or methane.

- Direct conversion of CO_2 to formaldehyde, which occurs via a stoichiometric reduction of CO_2 using zirconium metallocene $[Cp_2Zr(H)(Cl)]_n$ as a reducing agent (Heim et al., 2017). Formaldehyde can also be formed by reducing CO_2 using formate dehydrogenase (FDH) and formaldehyde dehydrogenase (FADH) as catalysts (Liu et al., 2014).
- Direct conversion of syngas to formaldehyde occurring in aqueous media, which causes the equilibrium to be pushed into a different direction. The produced formaldehyde is then stabilised as methanediol (CH_4O_2). This method is also known as direct hydrogenation of CO to formaldehyde (Bahmanpour, 2016).
- Direct oxidation of methane to formaldehyde in the presence of SiO_2 as a catalyst. At temperatures over 600 °C, free radicals are formed to initiate the process, which causes rapid reactions of formaldehyde formation in the gas phase (Bobrova et al., 2007). Metyhl radicals (CH_3) are first formed from methane and surface oxygen and are later converted to formaldehyde in the secondary interaction with surface oxygen.

3. Technology Readiness Level assessment

Guidelines for TRL assessment are available in the literature (Freeman and Bhown, 2011). In this study, the assessed technologies were assigned a TRL range based on information found in relevant research papers. Key indicator in the assessment is the production capacity of the processes, along with technology feasibility and viability. The first 3 levels denote technologies in the stages from basic principles observation to laboratory experiments (proof of concept). Levels 4-6 are technologies operating under realistic conditions up to pilot-scale experiments (proof of principle), and levels 7-9 are technologies on an increasingly larger commercial scale (proof of performance). The technologies and their respective TRLs are summarized in Table 1.

Table 1: TRL levels of formalin production technologies

Technology	TRL	Description
Formalin from natural gas	9	Actual system proven through successful operation in a commercial setting
Gasification of woody biomass or coal	9	Actual system proven through successful operation in a commercial setting
Syngas from black liquor	9	Actual system proven through successful operation in a commercial setting
Syngas produced via biogas	6	Pilot-scale system/subsystem prototype demonstrated in a relevant laboratory environment
CO_2 hydrogenation	8-9	Actual system proven through successful operation in a commercial setting
CAMERE process	6-7	Pilot-scale system/subsystem prototype demonstrated in a relevant laboratory environment
Electrocatalytic reduction of CO_2	3-4	Proof-of-concept validated through experiment or analysis
Reduction of CO_2 by other means	3	Proof-of-concept validated through experiment or analysis
Direct conversion of CO_2 to formaldehyde	2-3	Proof-of-concept validated through experiment or analysis
Direct conversion of syngas to formaldehyde	2-3	Technology concept and/or application formulated
Direct oxidation of methane to formaldehyde	2-3	Technology concept and/or application formulated

The current industrial processes for formalin production via steam reforming of natural gas are considered to be at the highest possible TRL. These processes include the routes of oxidation-dehydrogenation with complete or incomplete conversion of methanol using a silver catalyst and direct oxidation using metal catalysts. Of the other pathways which employ syngas for methanol production, several have been adapted to industrial-scale production plants. Black liquor is among the more advantageous gasification feedstocks due to its liquid properties, and Chemrec has utilized black liquor gasification technology to produce around 4 t/d of methanol (Landälv, 2007). Companies such as VärmlandsMetanol and Enerkem have used municipal solid waste (MSW) and woody biomass to produce biofuels at full-scale capacity (Methanol Institute, 2011). The biogas method to produce syngas and further methanol has been implemented in a pilot plant as a part of the WaStraK project (Ooms et al., 2017). Companies such as BASF and OCI/BioMCN have also utilized biomethane gained from biogas as a part of their feedstocks used to produce methanol (IRENA and Methanol Institute, 2021). However, there are still challenges related to this technology, mainly due to the difficulty in finding optimal operating conditions for the highest achievable methanol yield. As the ratio of CH_4/CO_2 in biogas varies depending on the source used (such as landfills gas recovery, wastewater treatment plants, MSW, agricultural and industrial waste, or other), the reforming process requires extensive optimization and testing.

Alternative pathways for formalin production have also matured to a high level, led by hydrogenation of CO_2 to produce methanol. Despite not being the main technology for methanol production, pilot operations as well as commercial processes producing around 4,000 t/y of methanol have already been developed (Richter, 2019). For the CAMERE process, a pilot plant with a production capacity of 100 kg/d of methanol has been constructed (Park et al., 2004). A notable advantage of this technology is that operating temperature is around 200 °C lower than for the CTM conversion technology. The key challenge of the CAMERE technology is catalyst selection, as a high conversion of CO_2 to CO is required, as well as stability at high temperatures. $ZnAl_2O_4$ is one catalyst that has shown effective activity and stability for the RWGS reaction (Aničić et al., 2014). Electrocatalytic reduction of CO_2 to methanol has been studied extensively in recent years, and offers advantages regarding energy consumption. However, due to low catalyst stability and incomplete research of reaction mechanisms, the technology has not matured beyond small-scale laboratory reactors (Liu et al., 2020). Direct electrocatalytic conversion of CO_2 to methanol is also likely ineffective as it has not been performed with sufficient methanol yields (Albo et al., 2015). Technologies where CO_2 is reduced by other means, such as the potentially sustainable methods of enzymatic and photocatalytic conversion, are in similar TRL range, as they face numerous challenges. The photocatalytic method has been difficult to apply due to a complicated mechanism, inefficient catalyst efficiency, and low product selectivity (Karamian and Sharifnia, 2016). Further development of these methods could present significant advantages, such as in the example of biological conversion to methanol, which can be carried out at ambient conditions (Patel et al., 2016).

Technologies for direct conversion to formaldehyde are generally at the lowest levels of maturity among those studied in this paper. Direct conversions of CO_2 (Nguyen et al., 2020), syngas (Bahmanpour, 2016) and methane (Tian et al., 2020) have all been reported at the laboratory level, but remain challenging due to major obstacles in catalyst and reaction mechanism design. In all three cases, further investigation of the reaction pathways is required for higher product yields.

4. Conclusions

This study reviewed progress made in developing the maturity of various formalin production technologies, based on the TRL assessment scale. It was found that alternative pathways such as CO_2 hydrogenation are already at a high enough level of maturity to produce methanol and formalin at a larger commercial scale. At a slightly lower TRL is the CAMERE process which is at the pilot stage of development. Technologies such as electrocatalytic reduction of CO_2 offer great potential to substitute current industrial processes. However, further technological development is required not only to ensure feasibility, but also to increase production capacity. Technologies for direct conversion to formaldehyde were found to be at the lowest TRLs. There is a need for further research of enzymatic or photochemical conversion, as these are clean technologies with the potential to conserve energy and reduce emissions.

In future research, the environmental and economic performance of formalin production technologies will be assessed to build on the knowledge gained in the TRL study. The results will enable a more detailed comparison between the technologies and offer a holistic view on formalin production. Combining the environmental, economic and technology maturity aspects will provide information to select the most sustainable technology for production of formalin.

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