

Methanol Synthesis – Industrial Challenges within a Changing Raw Material Landscape

Florian Nestler^{1,*}, Matthias Krüger², Johannes Full¹, Max J. Hadrich¹, Robin J. White¹, and Achim Schaadt¹

Worldwide production capacities of carbon-based chemicals and associated products are steadily increasing. At the same time the reduction of greenhouse gas emissions such as carbon dioxide is of paramount importance in order to mitigate the anthropogenic impact of climate change. In Carbon2Chem[®] a cross industrial network develops concepts towards the utilization of steel mill gases for the sustainable production of “green” base chemicals, including methanol. This Review describes the technological challenges emerging from the use of these alternative feedstocks, specifically in the context of methanol production processes.

Keywords: Carbon2Chem[®], CO₂ mitigation, Feedstocks, Steel mill gases, Sustainable methanol synthesis

1 Introduction

The use of fossil resources like coal, oil, and gas is known to be the main source for anthropogenic greenhouse gas emissions. At the same time there is an increased global demand for chemical products to cover the needs of a rapidly growing world population. New process routes and raw materials have to be identified that have the potential to harmonize global efforts to restrict emissions and establish sustainable chemical supply [1, 2]. Thus, over the last decade, many large-scale research initiatives were launched with the goal of replacing traditional industrial production by sustainable pathways [3–6]. These “green” chemicals are produced from renewable or abundant feedstocks such as biomass or waste streams and ideally driven by regenerative energies, e.g., solar, wind, or geothermal power.

As highlighted previously by Bertau et al. and Olah et al. among future base chemicals and energy carrier/storage systems, methanol is expected to play a key role [7, 8]. Methanol synthesis based on the conversion of syngas – a gas mixture containing hydrogen (H₂), carbon monoxide (CO), and carbon dioxide (CO₂) – has been commercially available for almost one century. The global demand for methanol is estimated by market researchers to grow steadily with a compound annual growth rate of 5.5 % until 2027. Methanol production is predicted to increase from 90 Mt in 2017 to 135 Mt in 2027 [9, 10].

Whilst state-of-the-art processes produce methanol almost exclusively from fossil fuels, there is an ever increasing interest in producing methanol based on alternative syngas sources. In such cases CO₂ and CO are obtained from industrial waste streams such as biogas plants, cement or steel production [3, 6, 11–13] or carbon capture from

air [14]. H₂ can be supplied from carbon-neutral sources, e.g., via electrolysis of water (H₂O). As with the integration of any new technologies, the use of these new syngas feedstocks and H₂ sources is likely to bring new challenges [12, 15]. In the scientific literature, numerous publications discuss the effects of synthesis conditions, reactor type or catalyst system on methanol synthesis sufficiently [16–25]. This review will highlight the challenges and opportunities faced by the chemical process industry concerning forthcoming methanol production based on sustainable feedstocks with a specific regard to steel mill process integration. In Sect. 2 process design basics and efficiency indicators for methanol synthesis are presented and discussed, later, with particular reference to conventional and alternative feedstocks respectively (Sect. 3 and 4). Finally, the main scientific and technological challenges as faced by emerging methanol production concepts such as Carbon2Chem[®] are discussed [6].

2 Technological Overview

In order to compare methanol process concepts based on different feedstocks, this section provides an overview of

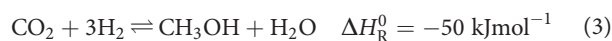
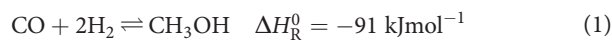
¹Florian Nestler, Johannes Full, Max J. Hadrich, Dr. Robin J. White, Dr. Achim Schaadt
florian.nestler@ise.fraunhofer.de
Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstraße 2, 79110 Freiburg, Germany.

²Dr. Matthias Krüger
thyssenkrupp Industrial Solutions AG, Friedrich-Uhde-Straße 15, 44141 Dortmund, Germany.

key indicators regarding the categorization of the syngas properties.

2.1 Process Fundamentals

Methanol synthesis on commercial Cu/ZnO/Al₂O₃ catalysts is macroscopically observed via the following reaction equilibria including CO hydrogenation (Eq. (1)), water-gas shift (WGS) (Eq. (2)) and CO₂ hydrogenation (Eq. (3)) [26]:



Radiolabeling studies by several research groups proved that methanol mainly originates from CO₂ hydrogenation, whereas CO hydrogenation does scarcely proceed [27,28]. Hence, CO conversion to methanol predominantly occurs via WGS with subsequent CO₂ hydrogenation.

A basic flow scheme of a methanol synthesis loop is provided in Fig. 1. The conditioned make-up gas (MUG) is mixed with gas from the recycle loop. The reactor feed enters the methanol reactor, where methanol is generated according to Eqs. (1), (2), and (3). Liquid raw methanol, i.e., a mixture of methanol, H₂O, and dissolved gases, is condensed and removed from the loop in a gas/liquid separator; with non-converted gas recycled. The recycle ratio is defined as the ratio between recycle flow and MUG flow. In order to avoid accumulation of inert components, a small portion of the recycle gas is purged from the loop. The higher the chosen recycle ratio, the lower the amount of purge gas. The raw methanol product is sent towards meth-

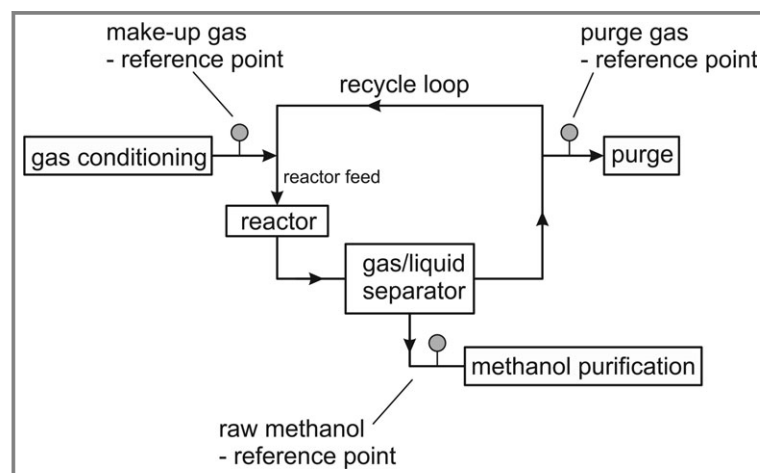


Figure 1. A basic process scheme of a methanol synthesis process with the main components and the reference points for the calculation of LCE, LHE_{intr} and LHE_{ext}.

anol storage and purification, typically realized by distillation. Syngas production will be described in Sect. 3.

2.2 Make-Up Gas Properties

The syngas quality plays an important role in the design of methanol synthesis processes. Four main factors can be considered concerning MUG composition.

2.2.1 Carbon Oxide Ratio

The methanol process can be designed for different ratios of the molar fractions of CO₂ (x_{CO_2}) and CO (x_{CO}) in the MUG. The carbon oxide ratio (COR) can be defined as follows [29 – 31]:

$$\text{COR} = \frac{x_{\text{CO}_2}}{x_{\text{CO}_2} + x_{\text{CO}}} \quad (4)$$

Based on the reaction enthalpies of Eqs. (1) and (3), the overall temperature rise in the reactor decreases with increasing COR. As an equimolar amount of H₂O is produced during the conversion of CO₂, H₂ consumption of methanol synthesis increases with COR. Several research groups observed that an increased H₂O content in the reactor enhances deactivation of the catalyst and decreases catalyst activity [21, 29, 32 – 34]. For these reasons in conventional applications, the COR is kept as low as possible.

However, as the direct hydrogenation of CO does scarcely occur on commercial catalysts, a certain amount of CO₂ needs to be present in the reactor feed to enable WGS and CO conversion to methanol [18, 21, 30, 31, 35 – 37]. A maximum methanol formation rate was experimentally observed by various researchers at a molar CO₂ concentration of approximately 2 mol.-% of carbon in the reactor feed [30, 31, 35, 38 – 45]. With a further increase in CO₂ content, the kinetics of the methanol synthesis is known to decelerate and the equilibrium yield decreases [46, 47]. The distribution and amount of side-products is also known to depend on the COR - typically more carbonaceous side-products are formed with decreasing COR [48, 49].

2.2.2 Stoichiometric Number

As the conversion of CO and CO₂ to methanol demands different molar ratios of H₂, a measure of the stoichiometry, the stoichiometric number (SN), is defined by the molar fractions of H₂ (x_{H_2}), CO and CO₂ in the MUG [20]:

$$\text{SN} = \frac{x_{\text{H}_2} - x_{\text{CO}_2}}{x_{\text{CO}} + x_{\text{CO}_2}} \quad (5)$$

For a stoichiometric conversion SN = 2 is necessary. Most methanol synthesis processes are

known to operate at slightly increased H_2 content [8, 50]. Nevertheless, some processes employ an excess of H_2 with $SN \leq 3$ (see Sect. 3.2). A high stoichiometric number can be lowered via the addition of CO or CO_2 , providing room for a capacity revamp. $SN < 2$ should be avoided, as a H_2 shortage in the syngas is known to promote the formation of undesired byproducts [7, 51].

2.2.3 Inert Gas Fraction

Inert gases are components that do not contribute to the synthesis reactions. Thus, their effect on the process design is limited to a dilution, in turn lowering the partial pressures of reactants. On the other hand, the presence of inert gases can be useful as their heat capacity lowers the temperature rise in the reactor. A high inert gas fraction in the MUG leads to an accumulation of inert components in the recycle loop, which has to be compensated by either increasing the recycle ratio or the purge ratio, in turn negatively influencing overall process economics [52, 53]. In order to minimize methanol production costs the inert gas content in the MUG should be kept as low as possible [54]. Common inert gases in the methanol process are nitrogen (N_2) and methane (CH_4), but also argon (Ar) or helium (He).

2.2.4 Impurities

In contrast to inert components, impurities in this article are referred to as all species originating from the feedstock and influencing the synthesis reaction, i.e. without being a main reactant. Most impurities have an inhibiting or deactivating effect on the catalyst, e.g., sulfur or chlorine [19, 21, 55]. Other than that, unwanted side-product formation can occur, for example the presence of ammonia is known to result in the formation of trimethylamine [56]. Specific countermeasures can be taken to cope with impurities, such as an enhanced upstream gas cleaning, a more complex downstream distillation unit or a higher catalyst volume.

2.3 Feedstock Comparison

The above described factors need to be considered for the technical implementation of methanol production and are strongly dependent on the nature of the feedstock used [8]. In order to obtain a syngas suitable for methanol synthesis the feedstock needs to be converted into an appropriate mixture of CO, CO_2 , and H_2 , satisfying the requirements mentioned above.

Fig. 2 visualizes the COR and inert gas fraction for various types of MUG. As the methanol synthesis process mainly depends on MUG composition, even different feedstocks can lead to the same design. Therefore, Fig. 2 is capable of showing if new feedstocks result in either new synthesis processes or if only adaptation of existing processes is

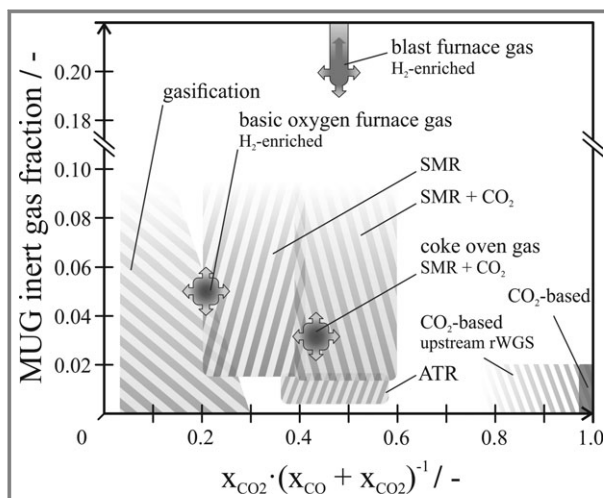


Figure 2. Comparison of estimated MUG compositions from conventional and alternative feedstocks means of their inert gas content and COR; Arrows indicate fluctuations in gas composition.

necessary. This simplifies the selection of synthesis loop parameters and helps to categorize different MUG compositions.

Inert components and unreacted syngas leave the process loop via the raw methanol and purge gas stream [57, 58]. Hence, an economical balance between recycle ratio and amount of purge gas has to be found for every individual scenario.

The loop carbon efficiency (LCE) indicates the ratio between carbon chemically bound in the raw methanol ($\dot{n}_{CH_3OH,Prod}$), to the overall amount of carbon oxides in the MUG, i.e., CO ($\dot{n}_{CO,MUG}$) and CO_2 ($\dot{n}_{CO_2,MUG}$) (Fig. 1) [59 – 63]. Carbon losses are mainly caused by purge, side-product formation and dissolved gases in the raw methanol. The LCE is expressed by the following definition:

$$LCE[\%] = \frac{\dot{n}_{CH_3OH,Prod}}{\dot{n}_{CO,MUG} + \dot{n}_{CO_2,MUG}} \cdot 100\% \quad (6)$$

The LCE is capable of comparing different loop designs and/or feedstocks. Carbon efficiency can be defined accordingly at other reference points, e.g., by the ratio of methanol production to the total amount of carbon bound in the feedstock.

For processes where H_2 is externally generated, another parameter describing the utilization of H_2 concurrent to the LCE is deemed reasonable [60, 64]. However, the definition of a loop hydrogen efficiency (LHE) is more complex. In addition to the above mentioned losses for LCE, it needs to be considered that H_2O is formed as inevitable byproduct from reactions Eqs. (2) and (3). There are two ways to evaluate the LHE:

1) An external LHE (LHE_{ext}) balancing the amount of H_2 solely bound in the methanol produced relative to the amount of H_2 in the MUG ($\dot{n}_{H_2,MUG}$):

$$\text{LHE}_{\text{ext}}[\%] = \frac{2\dot{n}_{\text{CH}_3\text{OH,Prod}}}{\dot{n}_{\text{H}_2,\text{MUG}}} \cdot 100\% \quad (7)$$

This definition is capable of comparing processes utilizing MUG with different COR. Gases with a high amount of CO_2 are less-favored as they demand for additional H_2 .

2) An internal LHE (LHE_{int}) considering H_2O in the raw methanol ($\dot{n}_{\text{H}_2\text{O,MUG}}$):

$$\text{LHE}_{\text{int}}[\%] = \frac{2\dot{n}_{\text{CH}_3\text{OH,Prod}} + \dot{n}_{\text{H}_2\text{O,Prod}}}{\dot{n}_{\text{H}_2,\text{MUG}}} \cdot 100\% \quad (8)$$

This definition is capable of comparing the efficiency of loop design independent of COR, equivalent to LCE.

In order to illustrate the above described key indicators, gas mixtures with varying COR are compared by means of their LCE, LHE_{ext} , and LHE_{int} in Fig. 3. LHE_{int} and LCE show a similar behavior. However, the increased H_2 demand of CO_2 -rich gas is only visible considering LHE_{ext} .

3 State-of-the-Art Feedstocks

As mentioned earlier, methanol synthesis is almost exclusively based on fossil feedstocks such as coal, crude oil and natural gas (NG). Despite growing coal-to-methanol capacities in China, 55% of the total installed production capacity is based on NG [10]. Independently of source, fossil feedstocks must firstly be converted into syngas via a gas generation process. Carbon-containing compounds, such as elemental carbon, CH_4 and higher hydrocarbons, need to be converted to CO , CO_2 , and H_2 .

The two main technologies used for syngas generation are gasification and reforming, see references [8, 54, 58, 65–67] for further details. This section continues with an overview on state-of-the-art feedstocks used for methanol synthesis, highlighting the respective properties of the generated syngas.

3.1 Coal, Biomass, and Refinery Residues

There are numerous solid and liquid feedstocks that are commonly used to prepare an appropriate syngas for the methanol synthesis [8, 67]. Among them are fossil products of natural coalification processes, including peat, lignite, bituminous coal through to anthracite – these are all typically gasified. Most residues from crude oil, like heavy oils naphtha, or liquefied petroleum gas (LPG) can either be gasified or reformed. Due to limited local availability and chemical heterogeneity, gasification of (municipal) waste and biomass can only be seen as a minor source for the production of methanol. However, benefits of their utilization are the potential mitigation of greenhouse gases and, in the case of waste, reduction of hazards associated with emitance to the natural environment.

All feedstocks differ in their chemical composition and impurity content. Accordingly, there are large numbers of different gas generation technologies, especially gasification schemes [68, 69]. Through natural carbonization, the amount of fixed carbon increases, whereas volatile compounds, especially bound hydrogen and oxygen, are outgassed. As a result, the produced syngas is sub-stoichiometric [67]. Hence, in order to adjust SN to the correct level, H_2 can either be added or the carbon oxide content can be decreased by shifting CO and subsequently removing surplus CO_2 . Typical MUG from coal gasifiers has an inert gas fraction between 1 and 6 %, predominantly of CH_4 .

Most syngas originating from biomass or fossil carbonization products typically contains many organic and inorganic impurities, making a comprehensive gas cleaning necessary. The main advantage of coal gasification processes is the inexpensive feedstock price compared to NG. As it is well distributed in the world, it is also geopolitically more independent, but entails drawbacks like vast H_2O demand, significantly higher CO_2 emissions arising from gas conditioning and elevated investment costs compared to a NG-based synthesis process [7, 58, 70].

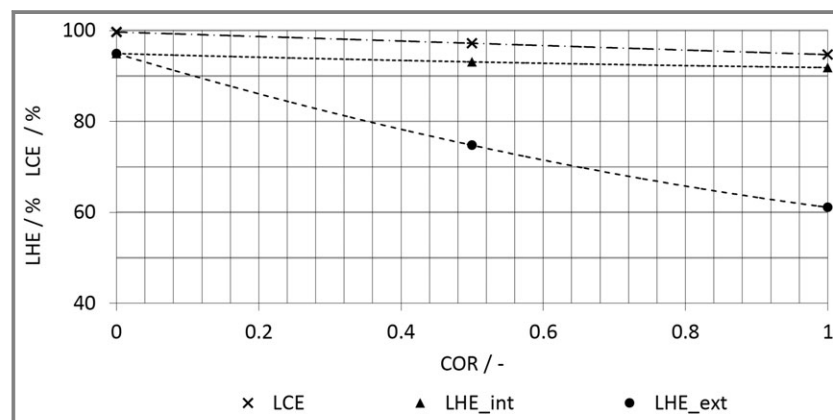


Figure 3. Comparison of LCE (x), LHE_{ext} (●), and LHE_{int} (▲) computed with varying COR at constant loop conditions and $\text{SN} = 2.1$.

3.2 Natural Gas

NG contains light hydrocarbons, mainly CH_4 , inert components (e.g., N_2) and impurities, such as sulfur-containing compounds or He. Besides ongoing efforts to develop methods for direct selective oxidation of CH_4 to methanol [71, 72], in commercial processes hydrocarbons are (catalytically) reformed into syngas. Steam methane reforming (SMR) is the most established route for NG-based feedstocks. However, there are also routes utilizing CO_2 such as dry reforming and bi-reforming [73]. Syngas produced by SMR usually contains

excess H_2 (SN from 2.5–3.0) [58,65]. External CO_2 can therefore be added in order to increase methanol capacity [54]. Steam reforming of higher hydrocarbons, however, can result in a H_2 -shortage.

The inert gas content of the MUG is determined by the N_2 content of NG and the CH_4 slip of the SMR reaction, with a value of 3–5% considered typical. As NG contains fewer impurities and is easier to handle than solid feedstocks, the gas cleaning is simplified compared to gasification processes. With the development of new reforming technologies, such as partial oxidation (POx) [54], autothermal reforming (ATR) [74,75], and combined reforming [65], the equilibrium of the reforming reaction has been increasingly optimized, resulting in a significant decrease of the CH_4 content in the MUG. These technologies also provide the possibility to adjust stoichiometry to the perfect level for methanol synthesis [54].

4 Alternative Feedstocks

Qin et al. have calculated a CO_2 equivalent of $2.97\ t_{CO_2,eq}t_{CH_3OH}^{-1}$ based on a cradle-to-gate life cycle assessment (LCA) of a coal-based methanol production plant in China [76]. For a NG-based process the according CO_2 equivalent amounts to $0.85\ t_{CO_2,eq}t_{CH_3OH}^{-1}$ [77]. In comparison, the direct hydrogenation of captured CO_2 to produce methanol (i.e., based on renewable electricity drive H_2O electrolysis – commonly referred to as “Power-to-methanol”) has been reported to have a CO_2 equivalent of $-0.67\ t_{CO_2,eq}t_{CH_3OH}^{-1}$. This implicates possible carbon emission savings of $1.52\ t_{CO_2,eq}t_{CH_3OH}^{-1}$ showing the sensitivity of methanol pricing towards political regulations such as taxation and trading systems [77,78].

The debate regarding the use and implementation of sustainable feedstocks and CO_2 -neutral processes for methanol synthesis arrived in the scientific community in the early 90s via contributions from both academic and industrial research groups [79–84]. As a consequence, new feedstocks are under discussion in order to find methanol synthesis concepts with increasingly lower carbon footprints. The following two sections introduce two types of alternative feedstocks: CO_2 point sources (e.g., biogas plants) and carbon oxide rich industrial off-gases that may arise from existing industrial processes (e.g., cement production). In this context, off-gases arising from steel production have significant potential, with particular respect to sector coupling and establishment of circular economies.

4.1 CO_2 -based Feedstocks

CO_2 -rich gas streams can be captured from industrial processes such as chemical or cement industry as well as combustion-based power plants [77]. Demonstration facilities at the small and industrial scale have led to enhanced knowl-

edge concerning the advantages and drawbacks of CO_2 -based methanol synthesis [57, 81, 84–89]. A benefit of a CO_2 -rich MUG for methanol synthesis is the lower heat duty emerging from CO_2 hydrogenation. Another advantage compared to conventional processes is the lower catalyst selectivity towards hydrocarbon side-products, e.g., ketones, leading to lower costs in product purification [32, 57, 81, 84, 90, 91]. The main drawbacks of CO_2 -based methanol synthesis arise from an increased H_2 consumption due to the formation of H_2O , leading to lower LHE_{ext} , equilibrium conversion and space time yield [57, 81, 92].

Besides catalyst research, industrial process solutions were developed allowing handling of CO_2 -rich MUG [15, 45, 79, 84, 93]. While some processes directly hydrogenate CO_2 to methanol [57], most of CO_2 -based process concepts condition the CO_2 -rich syngas by shifting CO_2 to CO via reverse WGS chemistry, e.g., the so-called CAMERE process [83, 87, 94]. A process concept proposed and indeed realized at a near industrial scale by Carbon Recycling International (CRI), also considers the option of a reverse WGS reactor in order to increase the CO content in the MUG [95].

The inert gas fraction for CO_2 -based processes is almost zero if an appropriate CO_2 removal is used in CO_2 capture. However, even with optimized process solutions the disadvantage of an elevated H_2 consumption persists [8]. This reinforces concerns linked to a sustainable H_2 supply which is known to be one of the core issues regarding future methanol synthesis [7, 86].

4.2 Steel Mill Gases

Compared to carbon capture and utilization (CCU) schemes, typically based on CO_2 -rich MUGs, gas sources with an elevated CO content increase the respective LHE_{ext} . Promising options in this context are gases emerging from steel mill processes [77]. The steelmaking industry (e.g., blast furnace processes) has the potential to provide large volume gas streams containing H_2 , CO and CO_2 . As such, a number of research initiatives aim to utilize steel mill gases for synthesis processes in order to decrease overall greenhouse gas emissions [4, 6, 96, 97]. Other routes for steel production with H_2 as reducing agent and electric arc furnaces are proposed by industry, but will not be further discussed within this review [98–100]. As the steel industry accounts for approximately 6.7 % of all global CO_2 emissions [101] ($1.9\ t_{CO_2,eq}t_{Steel}^{-1}$ are emitted on average through steel production [102]), it is reasonable to utilize “waste” process gases.

The compositions of three main types of steel mill gases, i.e., blast furnace gas (BFG), coke oven gas (COG), and basic oxygen furnace gas (BOFG), are provided in Fig. 4 [103]. With a fraction of approximately 87 % of the total volume of all gases, BFG is the predominant gas stream [104]. However, this gas stream has an inert gas fraction of ca. 50 %, in this case N_2 [6, 105, 106]. BOFG and COG have

smaller inert gas content, but cover only a small percentage of the total volume of all gas streams. Due to a high H_2 content, COG can be considered as a H_2 source [11, 107, 108], that can also be transferred to commercial syngas by conventional reforming technologies [64, 107, 109–112]. BOFG and BFG are both poor in H_2 (BFG: SN ≈ -0.40 and BOFG: SN ≈ -0.15) and therefore require additional H_2 to establish the correct SN (see Sect. 5). Another possibility of BFG utilization is the removal of CO_2 . In this case pure CO_2 is obtained and can therefore be processed with respect to Sect. 4.1.

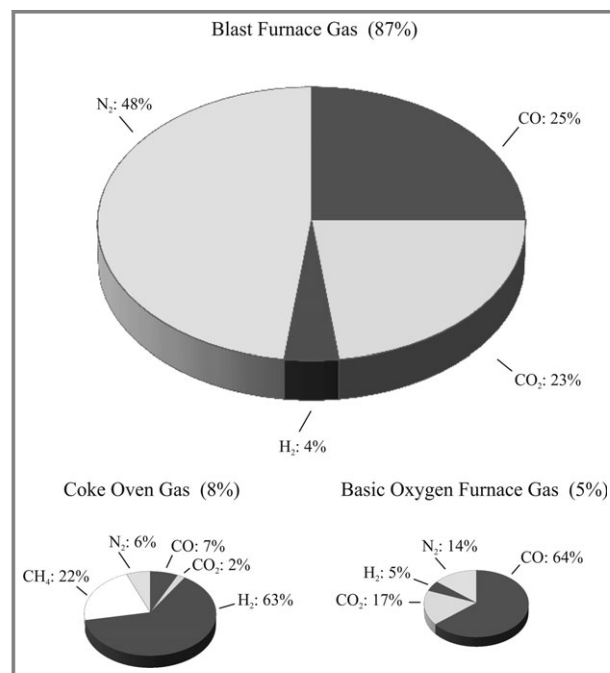


Figure 4. Gas composition of steel mill gas streams according to [103, 104]; Values in bracket give fraction of the total volumetric gas stream emitted from the steel mill.

Research projects concerning the utilization of steel mill gases are currently being funded in Europe, where reduction and recycling of CO_2 are major political goals (e.g., as supported by national initiatives [113]) creating new challenges for energy-intensive industries. One project initiated in this context by the European Union through the FP8/Horizon2020 “SPIRE” program is FReSMe, which is the follow-on of the previously funded MefCO2 and STEPWISE projects [3, 4, 114]. It focuses on CO_2 capture and methanol synthesis at a Swedish steel mill. A comparable project funded by the German Bundesministerium für Bildung und Forschung (BMBF) is Carbon2Chem[®] [6]. This initiative aims to utilize steel mill gases in order to produce methanol, but also higher hydrocarbons, ammonia, urea and polymers in a cross industrial or “sector coupling” network. The project collaborations Carbon2Value and Steelanol set a focus on Fisher-Tropsch synthesis and fermentation processes from steel mill gases [96, 97].

5 Challenges for the Methanol Synthesis Based on Steel Mill Gases

The aforementioned variety of MUGs derived from conventional and alternative syngas feedstocks clearly affects the design of methanol synthesis processes. Therefore, the utilization of steel mill gases will also demand the evaluation of alternative methanol synthesis concepts.

The focus for methanol production based on steel mill gases lies on the utilization of BFG and BOFG, as these cover the main fraction of all steel mill gases, i.e., ca. 92 % (see Fig. 4). Both raw gas streams provide an excess of carbon oxides, thus they need to be conditioned with additional H_2 , e.g., from H_2O electrolysis [115], CH_4 pyrolysis [116, 117] or internal sources such as COG.

In Fig. 2 the approximate compositions of conditioned steel mill gases (SN = 2.1) are shown in comparison to established and CO_2 -based feedstocks by means of inert gas content and COR. Mixtures of the streams were not considered, as Fig. 2 does not aim to deliver a process scheme, but rather to underline possible issues in methanol production from steel mill gases.

The H_2 -enriched BOFG and reformed COG offer a gas composition comparable to MUG from gasification or SMR, respectively. However, H_2 -enriched BFG shows distinct deviations due to increased inert gas content. Thus, the application of the standard synthesis process with BFG as MUG (Fig. 1) would either lead towards strongly elevated inert gas contents in the synthesis loop or elevated purge ratios with the consequence of decreased LCE, LHE_{int} and LHE_{ext} (Fig. 3). Loss of externally generated H_2 increases the cost of methanol production, whereas loss of carbon oxides negatively affects carbon footprint of the synthesis. Hence, as already proposed by other technical process concepts with enhanced inert gas content, application of a purge gas recovery [50, 118, 119] or once-through process cascades [120, 121] can be considered. Upstream gas conditioning can also be implemented to lead towards a more suitable MUG with decreased inert gas content.

Besides modifications in the methanol synthesis process, also modification in the cross-industrial network can be reasonable [122–124]. For example, operation of the blast furnace with O_2 -enriched gas instead of air is likely to increase steel making costs. But at the same time inert gas content in the MUG is reduced, allowing for application of state-of-the-art processes for methanol production [102]. Also options like partial conversion connected with downstream thermal recovery of unconverted purge gases can be a possible option. Co-production of methanol and nitrogen-based chemicals like fertilizers seem feasible and are therefore one major subject of Carbon2Chem[®] [6].

All steel mill gases are generated in industrial processes involving bulk solids such as coke, coal, ore, or scrap iron leading to a wide spectrum of organic and inorganic impurities. Thus, either impurities in the gases need to be removed by enhanced gas purification units [125] or cata-

lysts have to be developed that are more stable against poisoning.

Another challenge for methanol synthesis from alternative feedstocks is the fluctuation of upstream gas supply as a result of grid load compensation in case of renewable powered H_2 production and the dynamic behavior of the coupled industrial process [126]. Load-flexible operation is not yet state-of-the-art for methanol synthesis and only a few literature reports are concerned with the impact of fluctuating feed streams [127, 128]. Moreover, flexible operation decreases full load operating hours and can therefore negatively influence methanol production costs [77]. The impact of transient operation on catalyst lifetime and process units also needs to be considered [129]. A process concept capable of compensating temporary fluctuations of the MUG composition and quantity as well as new reactor models describing process dynamics must therefore be developed [127]. Some dynamics may be damped by an overall control scheme for the gas generation in the steel mill, power generation and chemical plant [122 – 124]. An expensive, but also feasible solution is the integration of gas storage systems. More advanced research will be necessary in order to describe flexible operation of the synthesis process and evaluate potentials and boundaries of dynamic process operation [128].

Furthermore, unlike conventional syngas feedstocks, steel mill gases demand a continuous obligation, as their generation is not determined by conventional methanol production planning, but rather the continuous operation of the steel mill. Another aspect to consider when steel mill gases are utilized is the possible conflict in use to direct thermal utilization, e.g. in turn potentially impacting on the overall efficiency of the cross-industrial network [125, 126, 130, 131]. Eventually further questions on a reasonable political framework need to be debated [78].

6 Conclusion and Outlook

This article compares the suitability of MUGs from conventional and alternative feedstocks for methanol synthesis. Key indicators are defined and discussed to identify pending issues, which need to be addressed in order to utilize steel mill gases. It was shown that these novel feedstocks offer a sustainable prospect to replace fossil feedstocks if combined with adequate H_2 supply. Aspects like the elevated inert gas content of BFG demand new process concepts in order to achieve maximum feedstock utilization and feasible process economy. Moreover, the effects of fluctuations in the MUG composition and quantity as well as impurities need to be addressed by the scientific community.

Although traditional feedstocks derived from fossil fuels may be the easiest choice for methanol production, the demand for energy and raw materials from alternative feedstocks is growing [7]. Large research projects are making promising moves in this direction. Relevant research data

will be generated by means of experimental studies, LCA and process simulation in the near future [100]. Indisputably these studies will lift alternative feedstocks for methanol production from a conceptual towards a technically feasible level. However, in order to implement these technologies into an industrial context, further political regulation will be necessary for these processes to be preferred over traditional, non-sustainable process routes.

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Florian Nestler is a graduate process engineer from Bingen University of Applied Sciences, Durban University of Technology and Dresden University of Technology. Since 2017 he is working at Fraunhofer Institute for Solar Energy Systems ISE. His current research topic is sustainable methanol synthesis with a focus on reactor design and process dynamics.



Matthias Krüger has graduated as Dr. rer. nat. from Ruhr-Universität Bochum, Faculty of Chemistry and Biochemistry. Since 2011 he has been working at thyssenkrupp Industrial Solutions (former thyssenkrupp Uhde) as senior process engineer in the Process Engineering and R&D Departments. His technological focus lies on syngas generation and applications, especially on methanol synthesis from fossil and renewable sources.

Symbols used

COR	[-]	carbon oxide ratio
ΔH_R°	[kJ mol ⁻¹]	standard enthalpy of reaction
LCE	[-]	loop carbon efficiency
LHE _{ext}	[-]	external loop hydrogen efficiency
LHE _{int}	[-]	internal loop hydrogen efficiency
\dot{n}	[mol h ⁻¹]	molar flow
S	[-]	stoichiometric number
x	[-]	molar fraction

Abbreviations

ATR	autothermal reforming
BFG	blast furnace gas
BMBF	Bundesministerium für Bildung und Forschung
BOFG	basic oxygen furnace gas,
C/H	carbon to hydrogen ratio
COG	coke oven gas
CRI	Carbon Recycling International
Cu-ZnO-Al ₂ O ₃	copper-zinc oxide-alumina
LCA	life cycle assessment
MUG	make up gas
NG	natural gas
OME	polyoxymethylene dimethyl ethers
SMR	steam reforming
POX	partial oxidation
PSA	pressure swing adsorption
SMR	steam methane reforming
TMA	trimethylamine
WGS	water-gas shift

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