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CO_2-based methanol and DME – Efficient technologies for industrial scale production

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ABSTRACT

The conversion of CO_2 with H_2 to methanol (MeOH) over a commercial Cu/ZnO catalyst (Süd-Chemie, Germany) was studied under process conditions. The obtained results showed a good stability of the catalytic system and a large potential for a CO_2 emission reduction with simultaneous production of MeOH or dimethyl ether (DME) as bulk chemicals or alternative fuels. If H_2 is obtained from renewable or CO_2-neutral sources (e.g. biomass, solar, wind or nuclear energy), respectively, a potentially CO_2-neutral cycle is possible. Compared to the conventional synthesis gas based technologies like the Lurgi MegaMethanol® process, the CO_2-based process shows lower productivities. However, since the overall reaction is less exothermic, lower temperature peaks and lower byproduct contents are found at similar process conditions. The higher purity is beneficial for further chemical conversions, like the DME synthesis. In the Lurgi MegaDME® technology, DME is produced efficiently in terms of costs and energy demand and can be used as alternative fuel for diesel engines. The MegaDME technology, based on the Lurgi MegaMethanol® process, allows overall capacities of up to 1.5 Mio t a^{-1} DME in a single process train from syngas generation via Methanol synthesis, to DME synthesis and product purification without parallelized equipment.

1. Introduction

1.1. Methanol from CO_2 and H_2

CO_2 can be both a blessing and a curse. While without it and other greenhouse gases, planet Earth would be a frozen world, due to burning of fossil fuels the CO_2 concentration has increased by 20% in the last 50 years [1] and is generally expected to result in significant and possibly irreversibly changes of the world's climate [2]. In 2005, approximately 28 Gt of CO_2 were produced and emitted by a variety of industrial and non-industrial fossil fuel consuming processes. Among those, the energy economy (i.e. power plants) produced almost half of this amount [3]. Ongoing discussions at governmental levels are attempting to develop a worldwide legal framework to maintain and then reduce the CO_2 levels in the atmosphere over the next 40 years.

Applying more energy efficient technologies or cars with lower petrol consumption can help to mitigate this problem. However, to limit the increase of CO_2 in the atmosphere, CO_2 has to be captured, sequestered or reused as a replacement for fossil fuels [3]. An interesting approach also favored by the Air Liquide Group is the chemical valorization of CO_2 by its conversion into methanol (see Fig. 1). Besides the MeOH formation reaction (1), the reverse water-gas shift reaction (2) as well as the CO hydrogenation to MeOH (3) can occur.

Methanol is a chemical commodity that is produced, traded and transported worldwide. Since Lurgi introduced its new ground-breaking MegaMethanol process for plants with a production of 5000 tonnes of methanol per day and more, methanol will be available at a constantly low price in the foreseeable future. The first Lurgi MegaMethanol® plant started up in fall 2004 and operates smoothly at 100%+ capacity since then. In the meantime four more plants have started up. This development has an enormous impact on downstream technologies for the conversion of methanol to more valuable products. Currently it is mainly used for further conversion, e.g. to formaldehyde, acetic acid or more recently also to propylene (via Lurgi's MTP® process), however, there is also a renaissance of its application as gasoline substitute. To date, more and more studies are published concerning the suitability of MeOH for gasoline blends, as well as concerning toxicology and environmental aspects of MeOH as a fuel [4–7].

Abbreviations: ALFE, Air Liquide Forschung und Entwicklung GmbH; CAPEX, capital expenditures; DME, dimethyl ether; EtOH, ethanol; GHSV, gas hourly space velocity; IGCC, integrated gasification combined cycle; LPG, liquefied petroleum gas; MeOH, methanol; MTP, methanol-to-propylene; MUG, makeup gas; RR, recycle ratio; STY, space-time-yield; TOS, time-on-stream; wt (-ppm), weight (-ppm).

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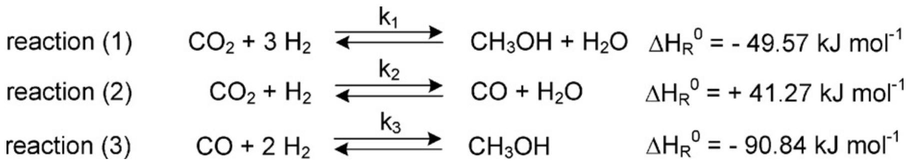

Fig. 1. Scheme of the reaction occurring during CO_2 hydrogenation.

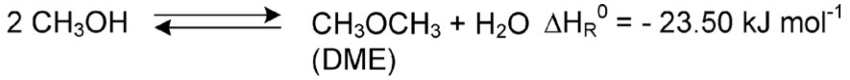

Fig. 2. Scheme of the DME formation reaction from MeOH.

To investigate the feasibility of the CO_2-to-methanol route, basically three questions have to be answered: (1) How to capture the CO_2? (2) How to produce the H_2 sustainably? (3) What does the CO_2-based methanol synthesis look like?

The detailed discussion of the first two questions is not in focus of this article and was already discussed elsewhere (e.g. [8–12]). However, it can be said that by application of oxycombustion (i.e. combustion with pure O_2 as oxidant instead of air) in power plants or blast furnaces a CO_2-rich flue gas can be generated that will simplify the separation and purification of the CO_2. Even simpler is the CO_2-capture in IGCCs (Integrated Gasification Combined Cycle) due to selective Rectisol® gas cleaning. Also, there are several options for H_2 production, both sustainable (non-fossil, e.g. photovoltaic or gasification of renewable feedstocks) [9–11] and conventional but non-fossil (such as nuclear) [12–14].

First studies of the CO_2-based methanol synthesis were carried out as early as the mid-90s [15–17] and described the catalytic and reaction system in terms of reaction kinetics, mechanism, catalyst development and scale up. However, this technology lay dormant in the years after. Only recently, due to the increased awareness to global warming and the proposal and implementation of cap-and-trade programs to regulate CO_2 emissions, interest has returned to this technology. While the syngas-based methanol synthesis is state-of-the-art, the adaptation to a CO_2-feedstock posed new challenges, such as development and testing of a suitable catalyst and the optimization of process parameters. Today's research is still focused on the development of catalytically active materials [18]. Studies about pilot plant operation and long term stability as well as the reaction mechanism are rather scarce [19,20].

1.2. Dimethyl ether (DME)

The first derivative of methanol in the presented context is DME which has a high potential as alternative to conventional diesel fuel, and as LPG (liquefied petroleum gas) supplement [21,22]. The conversion of methanol to obtain DME follows the sum reaction equation (see Fig. 2).

The process for converting pure methanol into DME is well known since decades: typically a γ-Al_2O_3 is used as catalyst and the moderate heat of reaction can best be handled in a simple adiabatic reactor set-up. Since the DME formation from methanol is a typical equilibrium reaction, the choice of reaction conditions is important. Depending on the temperature and the water content of the reactor inlet typically temperatures of 250–400 °C are applied to achieve per-pass methanol conversions of 70–85% (e.g. [23,24]). Therefore the process including reaction, workup, control, recycling, heat integration, etc. has to be carefully designed [25].

Within the present article recent developments in DME process technology at large scale are presented in Section 3.6 including a discussion about limitations and possible solutions by Lurgi.

2. Experimental

2.1. Setup for MeOH synthesis from CO_2

The experiments concerning the hydrogenation of CO_2 were carried out in a loop reactor with product separation and internal recycle (see Fig. 3). The makeup gas (MUG) was premixed and dosed into the reactor. The inlet gas was preheated and converted over a fixed bed of commercial MeOH catalyst pellets (Süd-Chemie, Germany). The resulting product mixture (H_2, CO_2, CO from reverse watergas shift reaction, MeOH and H_2O) was cooled and the liquid products were first separated under process pressure (i.e. 70–80 bar) and in a second step under near atmospheric pressure (i.e. 2–4 bar). The liquid phase was collected as crude MeOH product mainly comprising MeOH and water. The gas phase was recycled by means of a recycle compressor. The recycle gas was partly purged in order to prevent an accumulation of inert trace gases, especially when using standard syngas containing, e.g. CH_4 or N_2.

In order to obtain a complete characterization of the process, the mass flows or GHSV (gas hourly space velocities), pressures (p) and temperatures (T) as well as the compositions of the gas streams (MUG, solved and purge gas) and crude MeOH were monitored.

2.2. Continuous experiments

The experiments were carried out under conditions close to conventional process conditions of large scale MeOH plants (see Table 1). The water cooled tubular reactor used as fixed bed reactor was polytropic and showed a temperature profile with a temperature peak due to the exothermic MeOH formation reaction. The peak temperature observed during the test runs was mainly dependent on T, p, GHSV and the gas composition ($CO:CO_2$ ratio).

Prior to the long term test run the catalyst was reduced according to the manufacturer's prescriptions with diluted H_2 in N_2 (1%) at up to 250 °C. During reduction, the H_2 content was monitored in order to ensure complete reduction.

For startup of the setup, the premixed gas was dosed into the reactor until the final pressure of 80 bar was reached. During shutdown phases (e.g. over weekend) the catalyst was kept under inert atmosphere to prevent a reoxidation of the Cu surface.

3. Results and discussion

3.1. Activity and stability of the catalyst system

Catalytic production processes of bulk chemicals on an industrial scale are mainly dependent on the selectivity and stability of the catalyst. Low conversions are acceptable as long as unconverted substrate can be recycled with an acceptable effort. Therefore these aspects were in focus of the first characterization tests. The catalyst showed a good performance and yielded almost complete conver-

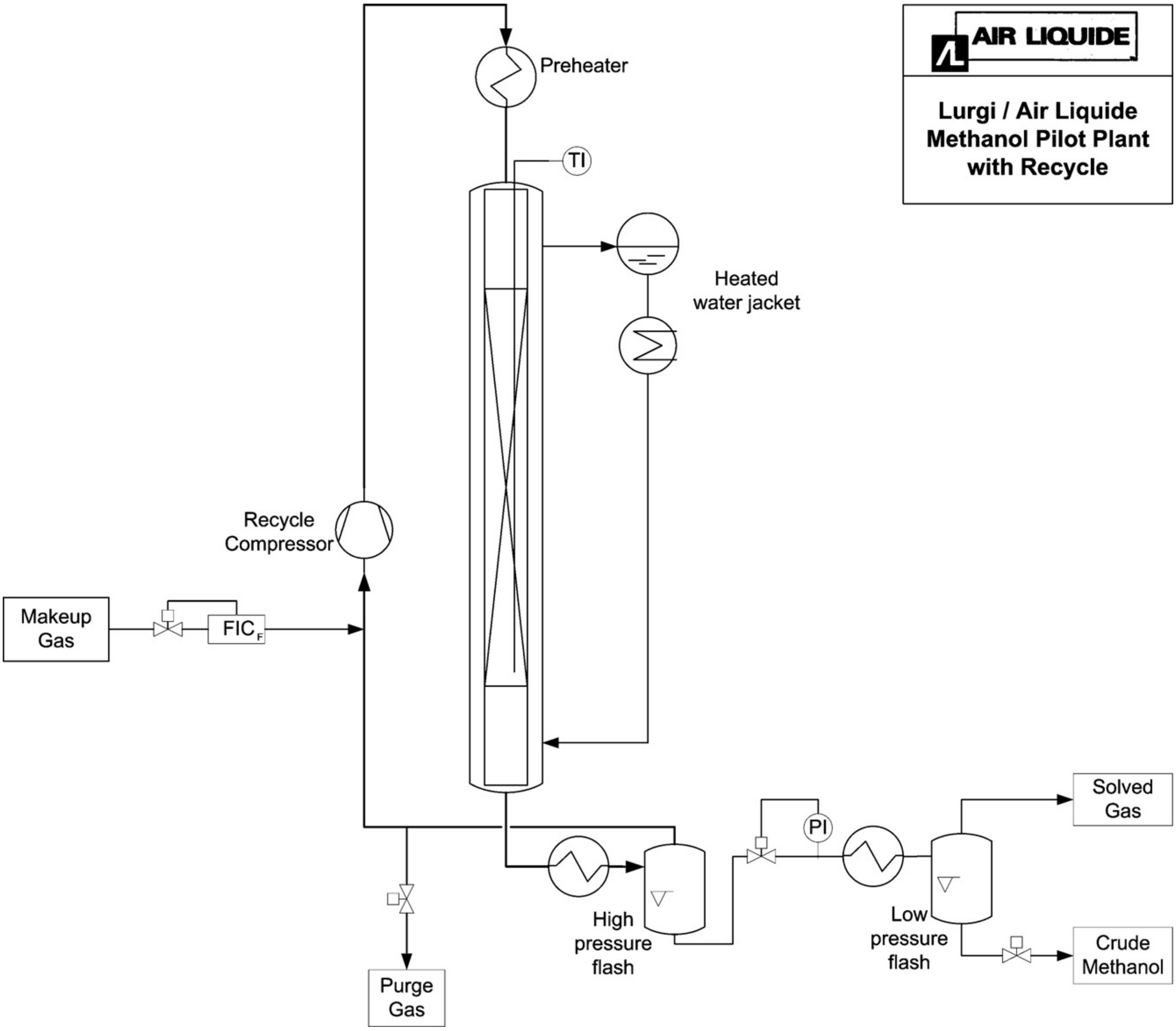

Fig. 3. Schematic picture of the PFD of the methanol pilot plant at the ALFE, Frankfurt, Main.

sion of CO_2. The CO_2 per-pass conversions were in the range 35–45% and showed a slight decrease over time-on-stream (TOS, see Fig. 4). The resulting deactivation rate was comparable to literature data (e.g. [16]). A direct comparison of the deactivation behavior for CO_2 syngas with standard CO syngas was not possible, but the observed deactivation rate for CO_2 syngas was in the same range as known for CO syngas. The reactor peak temperature (see Fig. 6) confirms the slow deactivation showing a significant change only during the formation phase (<100 h) and a stable temperature for the rest of the experiment. Up to now, no additional information about the deactivation behavior of the CO_2 system is available, mainly due to a lack of pilot scale studies and the resulting long term process data ($\gg$1000 h TOS). The data obtained within the presented studies do not allow an estimation of the overall catalyst lifetime, which is typically in the range of 3–5 years for standard syngas.

The per-pass conversions seem to be relatively sensitive towards startup and shutdown. Therefore the measured data do not show a clear steady state, not even after 150 h. Therefore, the conversions shown in Fig. 4 might not have reached their maximum and the obtained deactivation might be too fast and not transferable to a continuous operation without shutdown over weekend.

The productivity of the overall process (given as Space-Time-Yield, STY) is not only dependent on the conversions of CO_2 or CO in the reactor (influenced by T, p and the residence time) but also on the recycle ratio (RR), the product separation as well as the overall feed gas flow (as GHSV). The measured STY are in the range

Table 1
Experimental conditions of the long-term tests in the pilot plant.

Catalyst	Feed	Temperature		Pressure [bar]	GHSV [h^{-1}]	Test duration [h]
		T_{jacket} [°C]	T_{peak} [°C]			
Standard catalyst (Süd-Chemie)	CO_2-based	250	264–260 (see Fig. 6)	80	10,500	700
Standard catalyst (Süd-Chemie)	Standard syngas (CO-based)	250	283	70	10,500	100

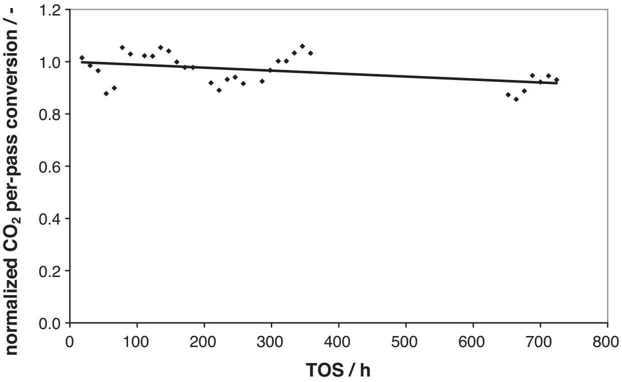

Fig. 4. Normalized CO_2 per-pass conversions over TOS, CO_2-based feed gas, experimental conditions see Table 1.

of 0.6 kg L_{cat}^{-1} h^{-1} (see Fig. 5) and show a slight decrease over TOS (3% relative decrease) during the first 100 h of operation ('formation phase'). During the following 600 h the STY virtually does not decrease further.

The obtained STY (see Fig. 5) are in the same range like reported by other groups. Typical STY are in the range of <0.3 up to 0.8 kg L_{cat}^{-1} h^{-1} [19,26,27] (see Table 2). The highest productivities were obtained for catalysts specially designed for the conversion of CO_2. The difference between the highest STY reported in literature and the STY found in our tests is relatively small. In addition, the main aim of the present studies was not the optimization of the overall process (reactor, catalyst, workup, etc.) but an evaluation of the potential of a CO_2 MeOH production process based on conventional technologies. With respect to all of these aspects, there is still room for improvement, e.g. based on adjusting the makeup-gas flow, *T*, *p* or RR.

3.2. Comparison with standard syngas-based reaction conditions

The process for the industrial scale low pressure MeOH synthesis is based on standard syngas, mostly obtained from natural gas, with excess of hydrogen – in case of pure steam methane reforming units – and rather low contents of CO_2 (mostly <10%). This process is known since the mid 1960s and is one of the most mature technologies existing in the field of chemical industry and production. Since this technology is so mature in terms of overall yield, product quality, catalyst lifetime and energy efficiency, novel technologies like the CO_2-based MeOH synthesis should make use of the developments of this state-of-the-art technology. In order to allow an accurate comparison between the two processes the long term test incorporated a period in which a standard synthesis gas mixture was used as feed gas keeping most other parameters constant, i.e. T, GHSV and the physical parameters of the product separation.

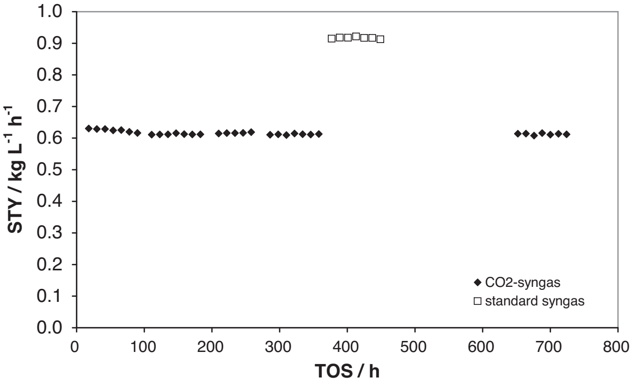

Fig. 5. Comparison of the STY over TOS for CO_2-based feed gas and standard syngas, experimental conditions see Table 1.

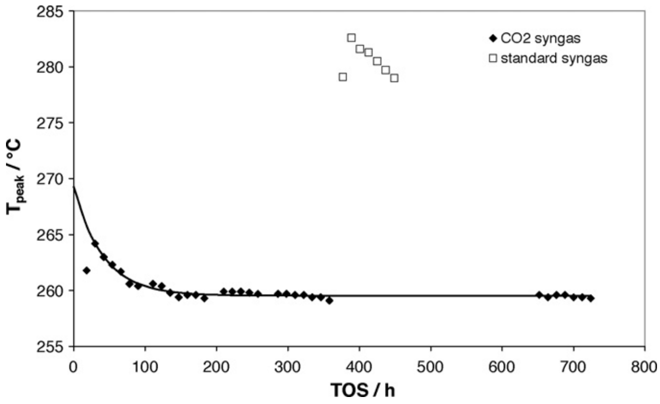

Fig. 6. Comparison of the peak temperatures for the hydrogenation of CO_2 and CO, experimental conditions see Table 1.

The pressure for the standard syngas experiment was decreased to 70 bar to avoid too high peak temperatures (see Table 1). The resulting peak temperatures inside the reactor during this test are shown in Fig. 6 and compared to the CO_2 experiments. The peak temperatures in the polytropic reactor are significantly higher (20 K approximately) when standard syngas is used. The higher temperature can be explained by the change of reaction in the system. If mainly CO_2 and H_2 are present, the predominant reactions are the CO_2 hydrogenation to MeOH and the reverse watergas shift reaction to CO and H_2O. If a CO-based syngas with a high ratio of CO:CO_2 is used, the main reaction is the CO hydrogenation (as sum reaction), which is significantly more exothermic than the other reactions. The higher exothermicity leads to an increase of peak temperature since the jacket temperature is kept constant at 250 °C. In addition, the CO conversion in standard syngas is known to be faster under the present process conditions [28,29] leading to sharper a T-peak.

As already mentioned before, the per-pass conversions are below 100% and the system is far away from equilibrium under the present conditions. In this case the productivity of the reaction system (STY) is mainly dependent on the reaction kinetics. Therefore the STY for the CO_2-based process are significantly (30–40%) lower than for the standard syngas-based process at lower pressure (see Fig. 5). However, the STY can be increased by suitable choice of process conditions. The most influential parameters are the GHSV, *T*, *p* and RR. In all cases specific limitations (e.g. pressure drop, thermal stability of the catalyst, equilibrium limitation, compressor power, etc.) have to be tested to assure full applicability of the respective conditions to the reactor setup or production plant.

3.3. Selectivity of the MeOH formation reaction from CO_2

Besides the catalyst activity and stability the selectivity is essential. In most industrial processes, the workup of the products is one of the most cost intensive parts of the overall production. In general, the MeOH synthesis reaction is already very selective. The crude MeOH product obtained from the low pressure flash of the pilot plant has a purity of 90%, approximately (if standard syngas is used as feed). The predominant byproduct is water with 10–12 wt.% produced by the CO_2 hydrogenation. This water can react with CO back to CO_2 and H_2 (watergas shift).

If CO_2 is used as feed gas, both primary reactions, i.e. the CO_2 hydrogenation to MeOH and the reverse watergas shift reaction to CO, are accompanied by a formation of water. Therefore, the crude MeOH from the CO_2-based process shows significantly higher

Table 2
Literature data for the CO_2 hydrogenation over various catalysts.

Reference	H_2:CO_2	T [°C]	p [bar]	GHSV [h^{-1}]	STY [$kg\,L_{cat}^{-1}\,h^{-1}$]	Comments
This work	3.1	250	80	10,500	0.6	Standard commercial catalyst (Süd-Chemie)
Saito et al. [26]	3.4	250	50	10,000	0.63 (after 1000 h)	MUG with 3% CO, Cu/ZnO/Al_2O_3/Ga_2O_3 catalyst, no recycle
Toyir et al. [27]	3.7	250	70	10,000	0.8	Cu/ZnO/ZrO_2/Al_2O_3/SiO_2 catalyst, with recycle
Doss et al. [19]	4.0	240	69	8500	0.07	Commercial catalyst, no recycle

Table 3
Purity of the crude MeOH product from the pilot plant.

Process conditions	Overall selectivity to MeOH [%]	Water content [wt.%]	Content of other byproducts [wt-ppm]
Standard syngas, 250 °C, 70 bar	87.0 (99.82)[a]	12.8	1800
CO_2-syngas, 250 °C, 80 bar	63.9 (99.96)[a]	36.1	390

[a] Excluding water and only taking the other byproducts into account.

water contents (30–40% water approximately). In both cases, the water content is strongly dependent on the CO_2 content in the syngas and additionally on the activity of the catalyst towards the (reverse) watergas shift reaction.

Apart from water as inevitable byproduct, other byproducts from parallel or consecutive reactions are present in significantly lower amounts. For standard syngas, the content of byproducts is in the range of 0.2%. The CO_2-based process yields MeOH in higher purity with 5 times lower byproduct contents (see Table 3).

This can be partly explained by the high temperature sensitivity of the byproduct formation reactions. These components are mainly formed at higher temperatures in the region of the temperature peak. Since the resulting catalyst bed temperature is higher when CO is present in the feed gas (see Fig. 6), the byproduct formation is faster, too.

However, in addition to this effect, also the conversion CO_2 seems to proceed with an inherently higher selectivity since the data in Fig. 7 show that even at comparable peak temperature levels of the reaction the byproduct formation is significantly reduced for CO_2-based syngas compared to the standard syngas.

It can be concluded that at similar process conditions the CO_2-conversion is slower but more selective. This allows the CO_2 hydrogenation to be run at higher temperatures without a major impact on the selectivity. Therefore the cooling need not be as intense as for the CO conversion.

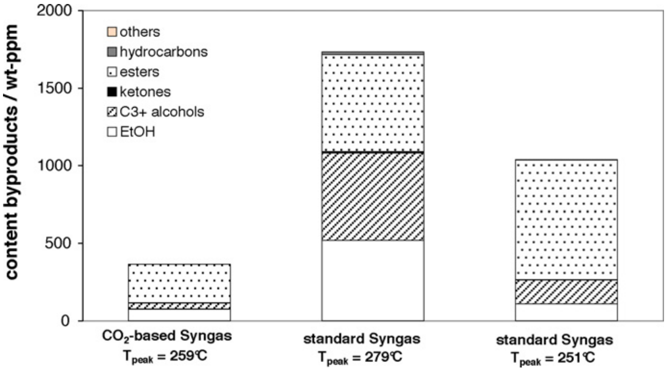

Fig. 7. Comparison of the byproducts in crude MeOH for various feed gas compositions and process conditions.

In principle, the product cleanup by distillation is mainly governed by the trace components and not by water as byproduct. The latter is easily separated from the crude MeOH, whereas other components can be more critical. Typically, some of the ketones (e.g. methylethylketone) form aceotropic mixtures that cannot be easily separated by distillation. In case of the CO_2-based MeOH synthesis, no ketones could be detected (content <1 wt-ppm). Therefore the distillation process is easier.

3.4. Simulation studies

In addition to the experimental studies of the CO_2-based MeOH synthesis, a process simulation based on a kinetic model (in-house expertise of Lurgi/Air Liquide) was used for the process evaluation as well as a first sensitivity analysis for the respective process parameters. The parity plot of calculated vs. measured gas composition (given as content of the single components at the reactor inlet and outlet) shows an excellent agreement (see Fig. 8).

In order to achieve a deeper understanding of the potential of the CO_2-based process, the process performance at various conditions was simulated. For clarity reasons, several scenarios can be defined: The ‘Base Case’ corresponds to the process conditions used in our measurements, i.e. CO_2 syngas at 80 bar, 250 °C and RR 4.5 and CO syngas at 70 bar, 250 °C and RR 3.6. This can be regarded as the combination ‘CO_2 syngas at CO_2 conditions’ and ‘CO syngas at CO conditions’. In addition, the alternative combinations were taken into account as well, i.e. CO_2 syngas at 70 bar, 250 °C and RR 3.6 (‘CO_2 syngas at CO conditions’) as well as CO syngas at 80 bar, 250 °C and RR 4.5 (‘CO syngas at CO_2 conditions’). The resulting productivities are found in Fig. 9.

It can be seen that for all cases the productivity of the process with standard syngas is higher than for the CO_2 hydrogenation process. The difference is 50% in the ‘Base Case’ both for the measurement and the simulation for these conditions. The higher productivity of the CO-based process can partly be explained by dis-

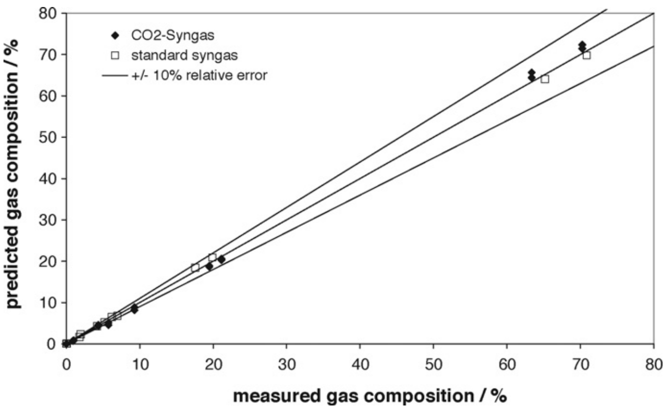

Fig. 8. Parity plot of calculated vs. experimental gas composition for CO_2-based feed gas and standard syngas.

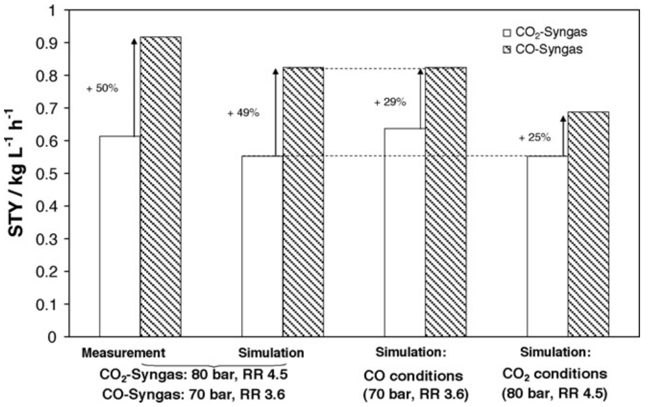

Fig. 9. Comparison of the STY for the CO and CO_2 hydrogenation at different process conditions.

advantageous process conditions for the CO_2 conversion. For 'CO conditions' in combination with CO_2 syngas (see Fig. 9) the simulation yielded significantly higher STY than for the 'Base Case'. For these conditions only 29% difference were found between the conversion of CO syngas and CO_2-syngas. For CO_2 conditions, the simulation results are even closer for both feed gas types. Under the respective conditions (i.e. 80 bar, 250 °C and RR = 4.5) the difference in STY for the two gas types is only 25%. From this it can be concluded that the MeOH production from CO is always more productive, but that the productivity difference can be significantly decreased by appropriate choice of process conditions.

When looking at the respective simulated temperature profiles (see Fig. 10), the temperature for the standard syngas is always higher. This will lead to a higher byproduct content and a higher thermal stress for the catalyst material.

In all cases one has to take into account that especially at low temperatures the STY is strongly dependent on the catalyst activity and not on thermodynamic equilibrium. In order to increase the productivity at such process conditions, catalyst systems have to be specially designed. The catalyst design was not in the focus of the present work. The aim was rather to test the applicability of conventional catalyst systems for the presented reaction system. Referring to this, the results clearly show the large potential of a CO_2-based MeOH production process already when a commercially available catalyst is used.

3.5. Startup behavior of the CO_2 hydrogenation

One characteristic property of the CO_2 hydrogenation being essential for the resulting process is the behavior during startup.

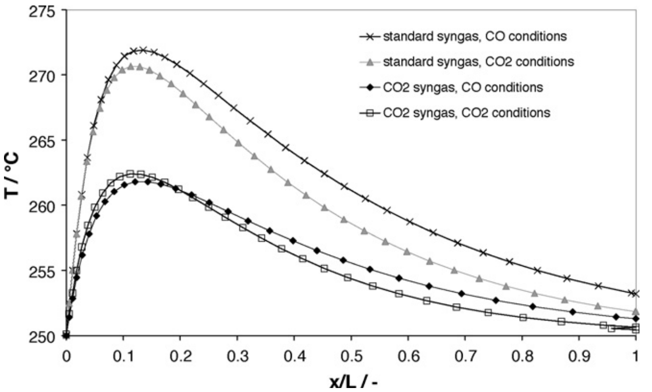

Fig. 10. Simulated temperature profiles for the CO and CO_2 hydrogenation, T_{jacket} = 250 °C, CO_2 conditions: 80 bar, RR = 4.5, CO-conditions: 70 bar, RR = 3.6.

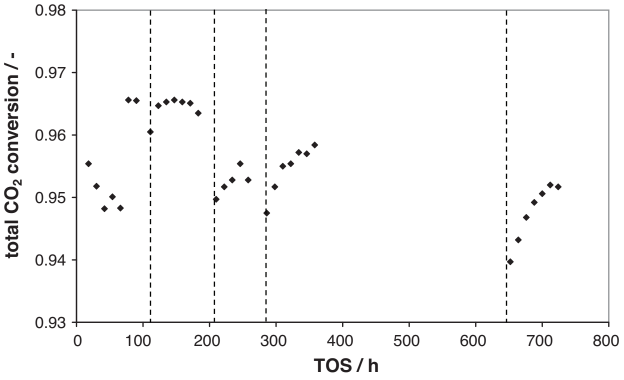

Fig. 11. Change of the total CO_2 conversion over time-on-stream showing the prolongated formation phases until steady-state; restart at 111 h, 210 h, 286 h and 652 h (indicated by dashed lines).

As shown by Goehna and Koenig [15], the time until steady state is reached is significant for the CO_2 hydrogenation and dependent on the process conditions. They found that at 80 bar, the formation phase lasts 80 h, approximately. For a process with continuous operation this formation phase can be neglected due to the very long catalyst lifetimes (typically > 2–3 years).

However, this formation phase may play a crucial role if the plant is operated under fluctuating conditions with regular startups and shutdowns. This would be the case if H_2 from fluctuating sources, e.g. from electrolysis with solar or wind energy [30,31], is to be used. In this context our results in fact showed a relatively slow increase of conversion after restart of the plant (see Fig. 11). This behavior might strongly influence the overall process.

So, although concepts for CO_2 valorization via MeOH synthesis with H_2 from alternative sources are not new, much still is to be done in this field of research.

3.6. The Lurgi MegaDME® process

The first and simplest "downstream" product from methanol is obtained by dehydration, two molecules of methanol yielding one molecule of dimethyl-ether (DME). This, aside from uses as chemical and propellant, potentially is a large scale energy carrier. It can supplement LPG (liquefied petroleum gas) and it can be used as transportation fuel, being a high cetane diesel alternative.

Typically a γ-Al_2O_3 is used as catalyst. The heat of reaction being significantly lower than in methanol synthesis causes the equilibrium to be less strongly influenced by temperature. This allows the use of simple adiabatic fixed-bed reactor setups for the industrial scale DME synthesis without a loss in conversion. Therefore the development of a new reactor design for this process was not within the focus of this work. While the two-step synthesis with MeOH as intermediate product requires more equipment than an integrated MeOH/DME process, at the same time it allows both reactions to be operated at their catalytic optimum. In addition, this concept benefits from the Lurgi expertise on both processes leading to a highly integrated and optimized overall process based on proven technologies [32].

Unlike the methanol synthesis, the 'volume neutral' formation of DME (see Fig. 2) is basically not affected by pressure. In this equilibrium limited reaction, typically 70–85% conversion of methanol per pass are reached at 250–360 °C, depending on the water content of the reactor feed.

Although the process for converting pure methanol into DME was well known since decades for the production of aerosol DME (e.g. [23,24]), it still could be improved, especially for large production capacities (i.e. >3000 t d^{-1}). When developing the new process

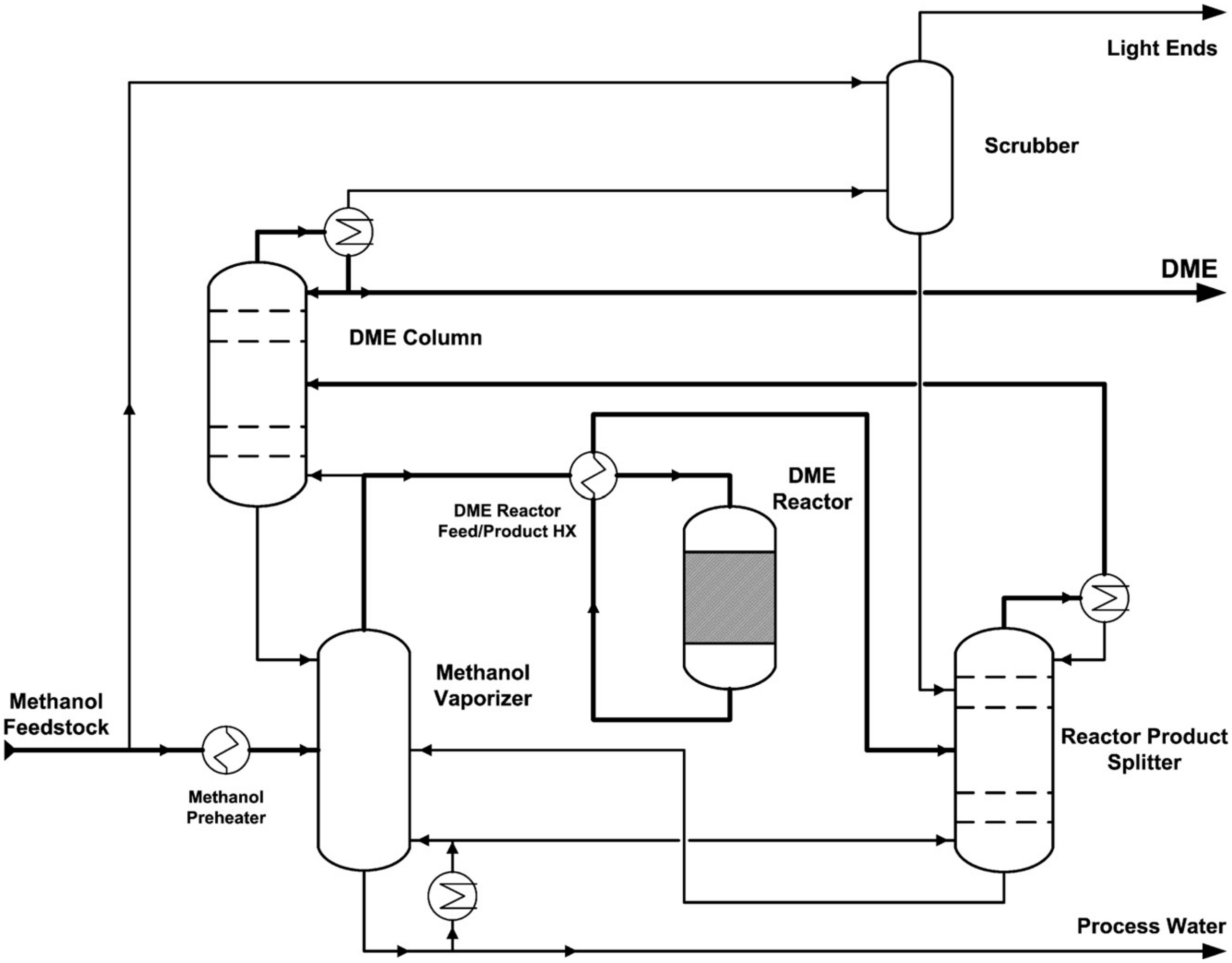

Fig. 12. MegaDME® basic process flow sheet (pat. pend. [25]).

flowsheet as depicted in Fig. 12, Lurgi adhered to the main principles of its MegaMethanol process, namely large single train capacity and high process and energy integration. The latter is achieved for instance by the coupling of two columns, the methanol vaporizer and the DME-column, so that each becomes the reboiler or overhead condenser of the other. This directly saves the investment cost for these two large equipments. In addition, the reboiler of the Methanol Vaporizer simultaneously acts as reboiler for the Reactor Product Splitter, again saving equipment and significantly decreasing CAPEX.

An important process and heat integration feature is indirectly incorporated in the utilized methanol feedstock. The Lurgi MegaDME® process can be operated using stabilized “crude” methanol as a feedstock opposed to conventional processes relying on pure methanol (i.e. methanol after distillation). Due to the combination of methanol vaporization and water separation in the Methanol Vaporizer Column, the Lurgi MegaDME® process (see Fig. 12) tolerates a considerably high amount of water in the feed methanol and in the recycle of the unconverted methanol. With this ability, the cost saving transformation of MegaMethanol into MegaDME is possible as depicted in Fig. 13.

While in the conventional DME process the large methanol distillation section is retained, it is no longer required in the Lurgi route, thus achieving important savings in investment cost and in energy consumption.

The above mentioned novel combination of heat integration, simplified purification as well as optimization for large scale makes the Lurgi MegaDME process so unique and opens the way for DME production on a thousand tons per day scale.

The investment cost and energy savings of the MegaDME technology were discussed in detail elsewhere [33,34] and can be quantified summarily as follows.

The investment cost for a natural gas based MegaDME plant is less than 10% above those of the corresponding MegaMethanol plant. Comparing conventional DME and MegaDME, the latter achieves DME production costs on energy basis 10–15% lower in the natural gas based case and 6–9% lower in the coal based case. In the market context this means that at a crude price in the region of 80–90 $ bbl^{-1} MegaDME can produce DME as an energy carrier (LPG supplement or diesel fuel) at highly competitive prices from natural gas and still competitively from coal.

3.7. Ecologic and economic considerations

The main attractiveness of the CO_2-based MeOH production is the reduction of overall CO_2 emissions, which can only be achieved if the required hydrogen can be provided from sustainable energy sources. The respective H_2 sources are currently investigated and potential process concepts have been developed already some decades ago. However, for a complete ecologic life-cycle evaluation all steps from the H_2 generation, the CO_2 separation and purification all the way to the methanol synthesis must be taken into account and analyzed. Given the complex influences and interdependence of raw material steams and purities, heat integration,

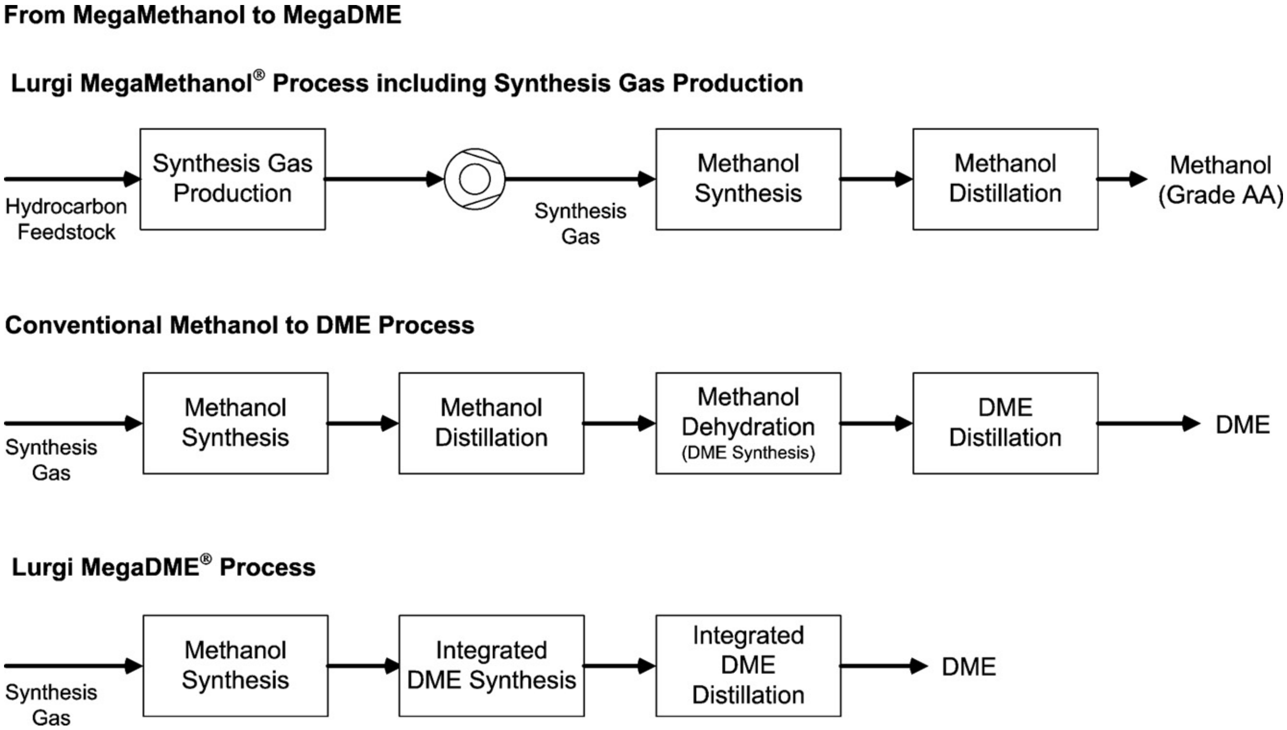

Fig. 13. From MegaMethanol to MegaDME.

steam import/export, use of byproducts, links to other processes, etc. this analysis is beyond the scope of the present article.

With respect to the economic feasibility of the process, the overall costs for MeOH of course depend on the price for CO_2 and H_2. Although both gases appear to be low cost products, their price will depend on the future energy market, technology developments and politics as well as technical requirement for CO_2 purification and H_2 generation. However, compared to conventional MeOH synthesis, the upstream syngas generation is no longer required which typically represents ~60% of the overall CAPEX of a MeOH plant which can be saved for the CO_2-based methanol process. In addition, the lower byproduct content of methanol produced from CO_2 may allow a simplified distillation.

4. Conclusion

The present studies concerning the conversion of CO_2 with hydrogen to MeOH over a commercially available standard $Cu/ZnO/Al_2O_3$ catalyst (Süd-Chemie) showed the potential of the resulting process. The CO_2 hydrogenation was slower than the CO hydrogenation under the described process conditions. However, the selectivity was higher and less byproducts were obtained when using CO_2 as carbon source. In a direct comparison with CO, the CO_2 hydrogenation is not competitive under the given conditions.

However, the large benefit of such an integrated and potentially CO_2-neutral process was shown. While it is understood that high purity CO_2 can be recovered and purified at a relatively low cost from many different sources, the production and/or recovery of high purity H_2 can be both a technical and economic obstacle to the development of any such projects. As long as the production of H_2 is based on fossil fuels, the environmental benefits of the process (CO_2 emission reduction) will be mitigated or limited. If instead, wind power, photovoltaic cells or excess nuclear power are used to produce hydrogen via electrolysis it can be used to produce methanol as energy storage medium and to reduce carbon emissions.

The basic MeOH production process was shown to be possible using a commercially available MeOH catalyst from Süd-Chemie. Concerning the final aim being a process including H_2 generation, CO_2 separation from potential sources, as well as the MeOH synthesis, still there is a long way to go until commercial application. However, CO_2-based processes with conventional technologies (e.g. H_2 generation) are possible already today.

Based on the MeOH produced this way, DME is a potential value-added downstream product. By using the novel Lurgi MegaDME® process, this product can be produced efficiently and cost effectively on a world scale basis.

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