INTEGRATING BIO-CO_2 WITH RENEWABLE HYDROGEN FOR THE SYNTHESIS OF MARITIME METHANOL

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ABSTRACT: Recognizing the growing emissions from the maritime sector and recent EU regulatory developments, this study explores the utilization of bio-CO_2 with renewable hydrogen to produce e-MeOH as a renewable maritime fuel. Process models are developed in Aspen Plus™, including a conventional single-reactor setup and a novel four-reactor configuration with intermediate cooling and separation. First, the performance of the conventional, once-through process is assessed through a sensitivity analysis, which demonstrates that maximum reactant conversion remains below 40% under typical operating conditions. Recycling improves conversion but causes inert buildup, leading to higher compression needs, larger equipment and slower response. The four-reactor system, by contrast, achieves higher conversion without recycling, reducing feedstock demand by 65% under once-through conditions. Finally, to assess the industrial relevance of the proposed technologies, three methanol production scales (150–600 tpd) are evaluated. Depending on those three production scales, 0.1-0.4 Mtpa of bio-CO_2 are required, indicating that only large bio-CO_2 emitters can meet this demand directly whereas smaller facilities would need to aggregate CO_2 at regional hubs. Green hydrogen requirements range from 13–150 ktpa (0.1–1.2 GW), indicating an additional limiting factor based on current EU capacities. However, future expansion of electrolyser technologies, CO_2 capture processes and planned EU initiatives could support e-MeOH adoption in the maritime sector.
Keywords: Biogenic CO_2, Maritime, Methanol, Renewable Hydrogen

1 INTRODUCTION

In 2022 the EU achieved a reduction of 31% on its net greenhouse gas (GHG) emissions compared to 1990 levels [1,2]. Over the same period, emissions related to the transport sector increased by 26%, with maritime transport accounting for 14.2% of the sector's total [3]. Recognizing the need to address CO_2 output in shipping, the EU included maritime measures in the Fit for 55 legislative package, such as extending the EU ETS system to include the emissions of all large ships entering EU ports [4]. At a global level, the International Maritime Organization revised its current GHG strategy to support zero or low emission fuels [5].

In these decarbonization efforts, the production of e-fuels suitable for maritime use through Carbon Capture and Utilization (CCU) has emerged as a promising strategy. This approach involves capturing CO_2 emissions, typically from industrial point sources or from the air, and combining it with renewable hydrogen to produce synthetic fuels [6,7]. Among e-fuels, methanol stands out for its favorable properties, compatibility with existing fuel infrastructure, and lower environmental impact if produced from renewable sources. Currently, methanol is widely used as a solvent and chemical feedstock, which means that safe handling procedures are already established [6,8]. Additionally, it exhibits similar characteristics to existing maritime fuels and thus requires minor infrastructure adjustments for transportation, storage and bunkering [9,10].

The utilization of biogenic CO_2 along with renewable hydrogen, could lead to achieving a small or even neutral carbon footprint for methanol production. Bio-CO_2 emissions originate from facilities that process biomass upstream, such as power, pulp and paper, bioethanol, biogas/biomethane, and food and beverage (FAB). These emissions are already part of the natural carbon cycle and do not induce additional stress to the atmosphere upon MeOH utilization. However, sourcing the required bio-CO_2 volumes is expected to be a key limitation since many of these sources are limited in number and capacity [11]. Additional challenges arise due to their dispersed and small-scale nature. This complicates capture and transport logistics, and can hinder the widespread adoption of such technologies. Competing demands further constrain supply, as bio-CO_2 is often reused on-site for example in the case of FAB industries (e.g. carbonation or food packaging) or diverted to the production of other products [12]. Another factor to consider is the composition of the resulting bio-CO_2 streams. Facilities such as biomethane, bioethanol and FAB plants involve high-purity streams (99-100 mol. %) but their relatively small emission volumes per site limit their individual contribution to the total bio-CO_2 sector. In contrast, biomass-fired heat and power plants and pulp and paper facilities are the two largest single-point sources of bio-CO_2 in the EU. Despite their scale, their CO_2 emissions are typically dilute (3-15 vol.%), since both sectors are associated with combustion-related upstream processes, which renders capture more energy- and cost-intensive [13,14].

The cost and availability of green hydrogen in large scales poses an additional challenge, since electrolysis requires considerable capital investments and, when directly integrated with renewable electricity, is restricted by lower capacity factors. An additional restriction is that conventional methanol synthesis is limited by equilibrium constraints, necessitating recycling to achieve higher conversions, which could lead to inert accumulation, higher compression needs, equipment sizes as well as slow dynamics of the integrated process. To this end, carefully addressing the bio-CO_2 value chain, optimizing renewable hydrogen utilization as well as increasing the efficiency of methanol synthesis are essential to establish e-methanol as a sustainable and viable maritime fuel.

This work examines the utilization of bio-CO_2 coupled with renewable hydrogen to produce methanol of maritime

specifications with a special focus on the modelling and simulation of the methanol synthesis system. Specifically, flowsheet simulations are conducted based on the conventional single- and a novel four-reactor setup with intermediate condensation and product removal steps. Different case studies are considered based on small- (150 tons/day), medium- (300 tons/day) and large-scale (600 tons/day) MeOH production capacities, to assess the short- to long-term applicability of this technology, illustrating the scales of bio-CO_2 and renewable hydrogen demands. The examined cases are evaluated based on key performance indicators such as feedstock requirements and reactant conversion.

2 PROCESS DESCRIPTION

2.1 Methanol synthesis process

In a conventional methanol synthesis setup, the fresh CO_2 stream and the green hydrogen (produced via electrolysis) are compressed to reach the reactor's operating conditions before being inserted into the reactor. The fresh mixture is mixed with the recycle stream (if recycling is applied) and preheated before being directed to the reactor where the following three reactions occur [15]:

$CO + 2H_2 \leftrightarrow CH_3OH$, ΔH^o = -90 kJ/mol — *Equation 1*

$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$, ΔH^o = -49 kJ/mol — *Equation 2*

$CO_2 + H_2 \leftrightarrow CO + H_2O$, ΔH^o = 41 kJ/mol — *Equation 3*

Methanol synthesis involves the exothermic hydrogenation of CO (*Equation 1*) and CO_2 (*Equation* 2), as well as the reverse water gas shift reaction (*Equation* 3), where CO_2 and H_2 react to produce CO and water. The first and the third reactions can be combined to form the second one, indicating an interdependency in the reaction system [8]. Additionally, the MeOH synthesis process is exothermic, leading to an increase in the gas volume, making it thermodynamically more favourable at low temperatures and high pressures (50-100 bar) [16]. However, practical limitations arise from kinetic constraints and catalyst requirements. The common $CuO/ZnO/Al_2O_3$ catalyst is activated at temperatures above 210 ^oC, while exceeding 280 ^oC can lead to catalyst sintering and deactivation [8].

For CO_2- and CO- containing feed streams, MeOH synthesis is characterized by the Stoichiometric Number (S.N.), (*Equation 4*):

$$S.N. = \frac{[H_2] - [CO_2]}{[CO_2] + [CO]} \qquad \textit{Equation 4}$$

Where [X] represents the molar concentration of reactant X (H_2, CO_2, CO) at the reactor inlet. If a pure CO_2 stream is used the stoichiometric number refers to the stoichiometric ratio of 3 between hydrogen and CO_2 (according to *Equation 2*). However, direct CO_2 hydrogenation processes produce CO as a by-product of the RWGS reaction. Therefore, when recycling is applied, CO returns to the reactor inlet and needs to be considered in the S.N. calculations. A value of 2 corresponds to stoichiometric conversion based on the combined hydrogenation of CO_2 and CO. Lower S.N. values limit conversion but could lead to higher hydrogen utilization rates, while higher values could increase conversion in expense of hydrogen excess [17]. Similarly to other studies, an S.N. of 2 is used throughout this work [18,19].

After the reaction, the product gases are cooled down and separated. Recycling the unreacted gas stream can be used to enhance conversion, along with a purge stream to control inert buildup within the system. Next, the crude methanol stream undergoes separation into two high- and low-pressure flash units, producing a liquid stream mainly composed of methanol, water and small quantities of unreacted gases. The stream is preheated and led to the distillation column to produce methanol of various specifications.

2.2 Multi-reactor configurations

Conventional methanol synthesis is restricted from equilibrium limitations, which result in reduced process efficiency and increased feedstock and energy demands. In the case of e-MeOH, the cost of acquiring renewable feedstocks can be much higher than its fossil-based alternative. To date, integrating a recycle stream has been the best alternative to address these challenges. However, recycling has shown to lead to the buildup of inerts, increase compression demands and equipment size, slow dynamic system response and increased by-product formation (Figure 5). To overcome these issues, a potential solution is to completely avoid the recycle operation by utilizing novel multi-reactor configurations that can enhance overall process efficiency even in once-through operation.

In the multi-reactor system, the pretreatment and purification sections remain unchanged. The difference is located in the synthesis section, where the gas stream leaving the high-pressure separator is reheated and fed to the subsequent reactor, with intermediate condensation and product separation applied between each stage (Figure 6). The removal of methanol and water improves reactant conversion, increasing MeOH yield and thus reducing the need for fresh CO_2 and H_2 feedstock [17]. In addition, since water is harmful to the catalyst and can lead to reduced activity over time, minimizing water content is expected to increase its lifetime [20]. By splitting the reaction into multiple stages, each reactor can be adjusted independently, allowing for better control and flexibility [19]. The reduced stream volumes associated with multi-reactor schemes also lead to smaller equipment size when it comes to the downstream purification of the crude MeOH product. More information on the benefits of the multi-reactor system can be found in previous works by the authors [17].

3 MODELLING METHODOLOGY AND ASSUMPTIONS

The methanol synthesis process is simulated in AspenPlus™, with the use of the Predictive Soave-Redlich-Kwong (PSRK) property package [21]. For the purification section the Non-Random Two Liquid (NRTL) property method package was used, with all non-condensable components treated as Henry components [22,23].

A bio-CO_2 stream composition of 99% purity was considered, reflecting typical post-capture purity levels, whereas trace impurities commonly found in bio-CO_2 streams are assumed to be effectively removed upstream, during the previous conditioning stages.

Green hydrogen is assumed to be produced through a

typical electrolysis (AEL) system. Hydrogen produced via AEL can reach up to >99.9% purity, after drying and oxygen separation. It also requires lower capital investment compared to other electrolyser technologies, with typical efficiencies ranging from 50% to 80% [24]. In this work, a 65% efficiency and a capacity factor of 80% are assumed, based on potential grid connection via a power purchase agreement [25].

The full set of assumptions and specifications used for defining feedstock conditions and simulating the methanol synthesis process, along with the KPIs used to evaluate it, are summarized in Table I.

Table I: Assumptions, feed specifications, and KPIs used for the methanol synthesis simulation.

Feedstock	Bio-CO_2	Green-H_2
Pressure, bar	1	30
Temperature, ºC	25	25
Composition, mol%		
CO_2	99	-
N_2	1	-
H_2	-	99.9
H_2O	-	0.1
Synthesis section		
Feed preheating temperature, ºC	210	
Reaction Temperature, ºC	200-280	
Reaction pressure, bar	50-100	
Stoichiometric Number	2	
High pressure flash, bar	50-100	
Recycling, %	0-90	
Purification section		
Low pressure flash, bar	1.2	
MeOH recovery, %	99	
KPIs considered		
Reactant conversion	$\frac{[X_{in}]-[X_{out}]}{[X_{in}]}$	
MeOH yield	$\frac{\dot{F}_{MeOH}}{\dot{F}_{CO_2,in}}$	

In this study the reactor is modelled based on two approaches; the thermodynamic and the kinetic approach. The thermodynamic model utilizes an RGibbs reactor block, considering CO_2, CH_3OH, CO, H_2, H_2O, and N_2 as possible products, with N_2 treated as an inert component [26]. The kinetic model was based on a multitube plug flow reactor using the kinetic rate expression developed by Vanden Bussche and Froment, with adjusted parameters by Mignard and Pritchard as described in the work of É. S. Van-Dal and C. Bouallou [27]. Key specifications included a bed voidage of 0.3, catalyst density of 1770 kg/m^3, tube diameter of 0.025 m, tube length of 5 m, a gas hourly space velocity (GHSV) of 10,000 h^{-1}, and pressure drop calculated using the Ergun equation. Simulation results indicated that, under the studied conditions, the two modeling approaches result in a deviation of less than 5%. Given this, the thermodynamic model was selected for use in all subsequent simulations.

4 RESULTS

4.1 Methanol synthesis process and improvement

Figure 1 (a) and (b) show the influence of reactor operating conditions on CO_2 and H_2 conversion, respectively, based on the conventional methanol synthesis process (depicted in Figure 5). As expected from reaction thermodynamics and stoichiometry, lower temperatures and higher pressures improve reactant conversion. At elevated temperatures, CO_2 conversion tends to stabilize and slightly increase due to the endothermic nature of RWGS reaction. This is further validated in Figure 1 (c) which shows the reduction of the MeOH yield index under high temperatures indicating lower methanol production and increased water formation.

However, selecting the synthesis conditions requires consideration of the catalyst operating conditions, since the $CuO/ZnO/Al_2O_3$ catalyst requires elevated temperatures for activation. At the same time, higher temperatures (>280 ºC) decrease efficiency and deactivate the catalyst due to sintering [8]. Considering these limitations, a moderate synthesis temperature of 250°C and pressure of 70 bar was selected for the subsequent simulations.

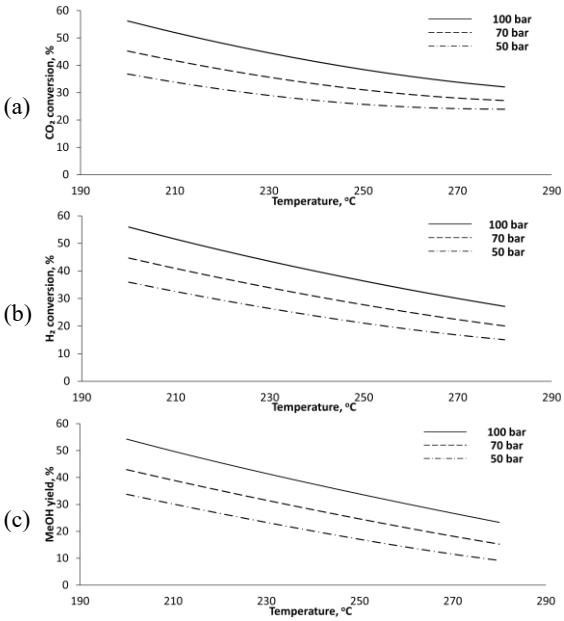

Figure 1: Thermodynamic limitations of reaction conditions on: (a) CO_2 conversion, (b) H_2 conversion and (c) MeOH yield.

The temperature-pressure analysis clearly highlights the limitations of the once-through, single-reactor operation, as the maximum attainable conversion is restricted to below 40% under the considered conditions (250 ºC and 70 bar). This means that a large portion of the introduced feed remains unutilized, making essential the incorporation of a recycle stream.

As shown in Figure 2, recycling of unconverted gases helps overcome equilibrium limitations, increasing conversion-utilization and decreasing the specific feed requirements for methanol production.

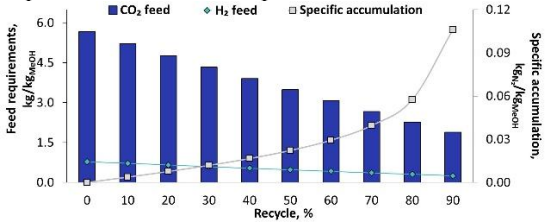

Figure 2: The effect of recycle % on specific feed requirements and on specific accumulation.

Specifically, recycling 90% of the separated product gas stream results in a reduction of the required fresh CO_2 and H_2 feed rates by ~68%, compared to the once-through operation. The benefits of recycling are accompanied by challenges related to the accumulation of inert gases. High recycle ratios can lead to a significant increase in the volume of Nitrogen being recirculated, as shown from the exponential rise in its specific accumulation in the recycle stream (Figure 2). For unconventional feedstocks with higher inert contents, this trend is even more apparent leading to significant inert accumulation rates [28,29].

Figure 3 illustrates the specific feedstock requirements for e-MeOH synthesis comparing configurations with one or four reactors operating in once-through mode at the selected conditions (70 bar, 250 ºC). The results show that the novel multi-reactor scheme (illustrated in Figure 6) leads to significant improvements in reactant conversion-utilization and thus reduces the required feedstock for methanol production. This is because the integration of intermediate cooling and product separation shifts the chemical equilibrium towards further reactant conversion, promoting methanol synthesis in each reaction stage. Specifically, the once-through four-reactor scheme results in 65% reduction in feedstock requirements compared to the conventional once-through, single-reactor operation.

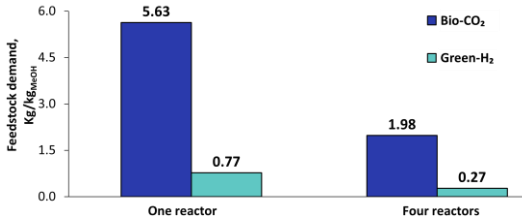

Figure 3: Multi-reactor effect on bio-CO_2 and green-H_2 requirements.

4.2 Bio-co$_2$ and hydrogen integration

Constraints in sourcing renewable feedstocks, such as the limited capacity of bio-CO_2 sources and the large-scale employment of the green hydrogen production infrastructure and market, necessitate assessing whether industrial methanol production scales are feasible under current and future EU capabilities. To ensure a realistic assessment, simulations are conducted across a range of potential industrial production scales: i) 150 tons of MeOH/day, ii) 300 tons of MeOH/day, and iii) 600 tons of MeOH/day.

Figure 4 presents the feedstock requirements for the three case studies, while the results for the main streams of the first case are illustrated in Table II. The findings suggest that for the considered scales, significant volumes of both bio-CO_2 and green hydrogen are required. Specifically, the production of 150-600 tons of MeOH/day through the conventional scheme, requires between 0.3 and 1.1 Mtpa of bio-CO_2. Compared to average emissions from bio-CO_2 plants, these volumes could be potentially covered by large-scale emitters such as combustion and pulp and paper plants, whereas smaller scale facilities will need to gather bio-CO_2 from different plants in order to reach the required quantities. Overall, the use of the multi-reactor configuration improves the efficiency of the process, helping reduce feedstock demand to 0.1-0.4 Mtpa, compared to the single reactor, once-through operation.

Green hydrogen requirements are also substantial, particularly when compared to current production capacities. Operating a small- to large-scale e-methanol facility would demand between 13 and 150 ktpa of renewable hydrogen (depending on the employed scheme) which correspond to 0.1 – 1.2 GW of installed electrolyser capacity, with current installations in EU being limited to 385 MW [30].

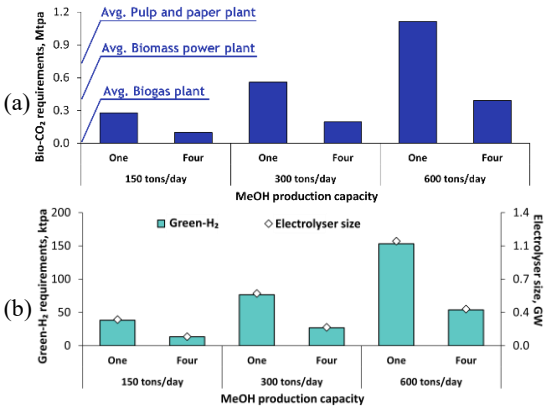

Figure 4: (a) Bio-CO_2 and (b) Green H_2 along with associated electrolyser size requirements across the three case study plant capacities.

Advancements in CO_2 capture and electrolyser technologies are expected to expand the availability of renewable feedstocks, supporting the large-scale production of e-MeOH. The EU has set a target of producing 10 Mtpa of green hydrogen by 2030 [31]. This could enable the large-scale production of e-MeOH, provided that sufficient volumes of bio-CO_2 are captured.

5 CONCLUSIONS

This study demonstrated that integrating bio-CO_2 with renewable hydrogen offers a viable pathway for producing e-methanol suitable for maritime applications. The results showed that conventional single-reactor systems are limited by thermodynamic constraints, resulting in reactant conversion rates below 40% and making gas recycling necessary. The proposed four-reactor once-through configuration overcomes these challenges, significantly improving MeOH yield and reducing feedstock requirements by 65%. The case study analysis revealed that large-scale deployment requires significant quantities of bio-CO_2 (0.1-1.1 Mtpa), making single-source supply feasible for high-capacity emitters such as pulp and paper and combustion plants. Green-H_2 demands, estimated to be between 13-150 ktpa (0.1-1.2 GW) represent an additional constraint given the current limitations in EU electrolyser capacity. Future work will focus on assessing the entire maritime e-MeOH value chain, along with dynamic modelling and optimization of the methanol synthesis process.

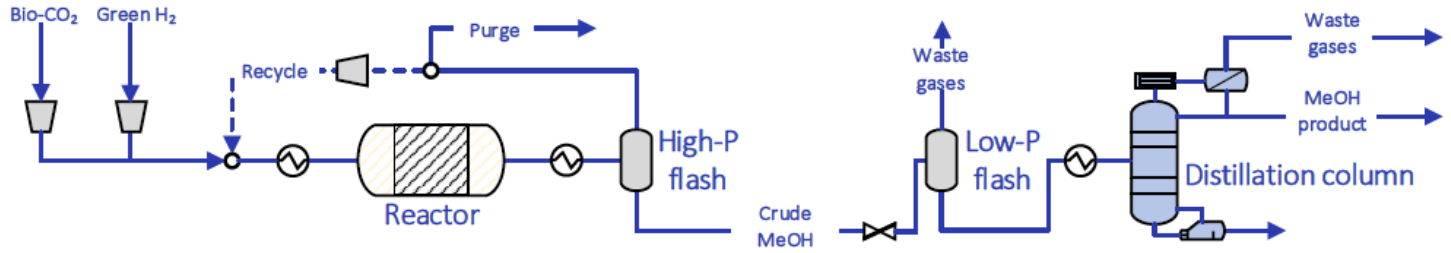

Figure 5: Simplified flowsheet of the conventional single-reactor configuration with recycling.

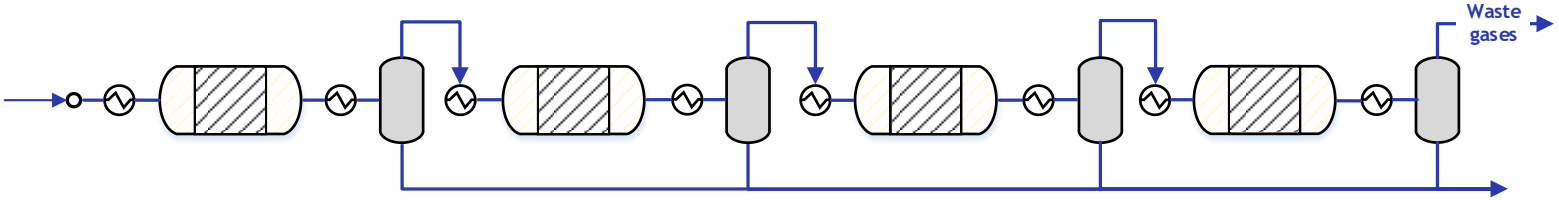

Figure 6: Flowsheet of the synthesis section for the four-reactor, once-through configuration.

Table II: Main stream results for the examined once-through four-reactor synthesis scheme based on the small-scale (150 tons/day) case study of e-MeOH production capacity.

Configuration	Four-reactor, once-through scheme				
Stream name	Bio-CO_2	Green H_2	Reactor inlet	Crude MeOH	MeOH product
Total mass flow rate (kg/h)	12,450	1,715	14,165	10,646	6,300
T, K	298	298	483	308	303
P, bar	1	30	70	70	1
% mol fraction					
CO_2	99.0	0.0	24.9	2.8	0.2
CO	0.0	0.0	0.0	0.0	0.0
H_2O	0.0	0.1	0.1	49.2	0.9
H_2	0.0	99.9	74.7	0.7	0.0
N_2	1.0	0.0	0.3	0.0	0.0
CH_3OH	0.0	0.0	0.0	47.3	98.9

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