Analysis of the Main Production Routes of Biomethane and Dimethyl Ether (DME) from Biomass

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The present work comprehensively analyzes the technologies and processes involved in producing dimethyl ether (DME), from biomass gamification to biomethane synthesis. For this purpose, the technical aspects of the operational parameters must be addressed. This study aims to analyze the efficiency and technical feasibility of the main production routes of DME using biomass. The method used in this work is based on a comparative analysis of the significant DME production roads, comparing them through a systematic bibliographic review. The results suggest using more efficient routes, focusing on greater efficiency, biomethane quality, selectivity, and CO_2 reduction.
Keywords: Production of Dimethyl Ether. Biomethane. Biomass.

The growing interest in renewable fuels such as biomass is linked to environmental sustainability and the need to reduce reliance on conventional fuels. Exploiting alternative sources such as biomass, biomethane, and dimethyl ether (DME) from biomass presents a promising path to sustainable biofuel production. Sources of biomass for biomethane production include organic materials such as lignocellulosic biomass, agricultural, urban, and forestry, and energy-intensive crops such as corn, beet, sugarcane, and sweet sorgo, among others [1].

Dimethyl ether (DME) is a chemical compound widely used in industries as a propellant, serving as a substitute for diesel and oil gas (GLP). It can be synthesized from coal, oil, and biomass, including greenhouse gases. Known for its exceptional cleanliness and compressibility, the DME offers a promising alternative to diesel and GLP as a source of energy, both for combustion and as an energy source fuel, due to its self-ignition capacity and impressive octane index [2,3].

Biomass is a renewable source with great energy potential, used for power generation as a fuel, with excellent energy properties, low CO_2 emissions, and long-term economic advantages. The biomethane production process includes pretreatment, gasification, synthesis gas cleaning, hydrocarbon reforming, adjustment of the H_2/CO ratio, and biomethane synthesis [2].

Biomethane and DME Conversion Routes

Description of the main Biogas and Biomethane Production Routes

Biogas production mainly involves anaerobic digestion and thermal gasification [4]. Anaerobic digestion is a complex process that requires strict anaerobic conditions and microbiological activity to convert organic material into biogas, primarily composed of methane and carbon dioxide [5]. Thermal gasification, or thermochemical conversion, is influenced by temperature, pressure, and gasifying agents. The resulting biogas can be used for heating, electricity generation, and as a fuel for vehicles [4].

Biomethane to DME Conversion Processes

Biomass gasification involves gas cycling, refrigeration, and purification units directed to a synthesis gas reactor. After condensing and separating the gases, the gas is synthesized from its elementary components, suitable for use in transportation, power generation, industrial applications, and additional chemicals [7].

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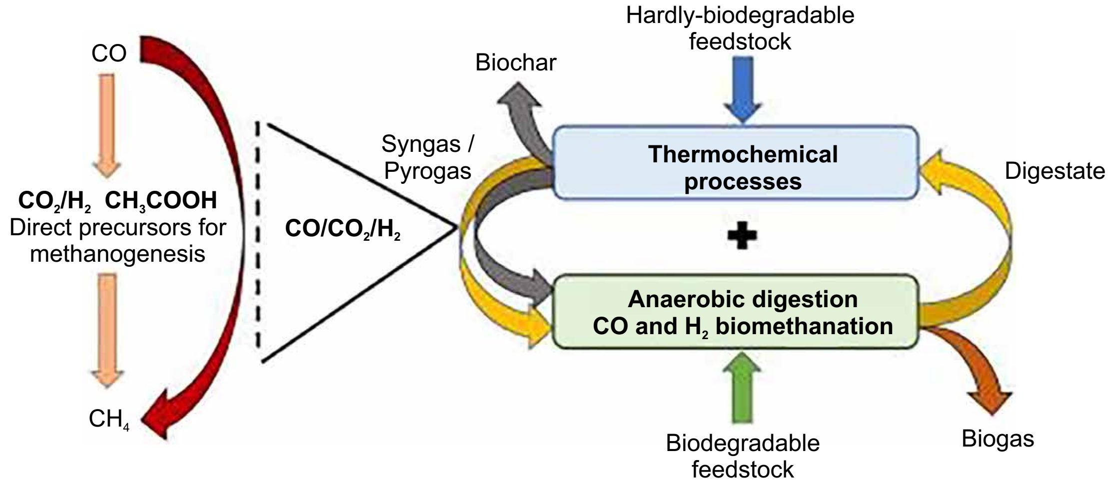
Figure 1: Biogas conversion and production by anaerobic digestion and thermochemical processes.



Source: Andreides and colleagues (2022) [6].

Dimethyl Ether (DME) Production Routes and Their Steps

The main processes for producing dimethyl ether from biogas include direct catalytic hydrogenation of CO_2 and the synthesis of DME from biomass-derived syngas [2,8]. The synthesized gas is converted to methanol using synthesis reactions, with CO reacting with water steam (H_2O) to generate CO_2 and H_2, followed by catalytic dehydration and fusion of methanol to form DME, according to the sequence of the following equations [9]:

Methanol formation: $CO + 2H_2 \leftrightarrow CH_3OH$ DHO = -90.4 kJ/mol (1)
Water-gas change: $CO + H_2O \leftrightarrow CO_2 + H_2$ DHO = -41.0 kJ/mol (2)
Methanol dehydration: $2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$ DHO = −23.0 kJ/mol (3)
General reaction: $3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2$ DHO = −258.3 kJ/mol (4)

Direct Biomass Synthesis Route

The direct pathway of DME synthesis involves partially hydrogenating carbon monoxide (CO) and the DME synthetic reaction. In the direct catalytic hydrogenation process, CO_2 is converted to methanol using bifunctional/hybrid catalyst systems, which combine metal and acid functions. Methanol is then dehydrated to DME using an acid catalyst (Figure 2) [10,11].

Route Indirect Synthesis Via Synthetic Gas

The methanol dehydration process is a necessary step in producing dimethyl ether. The DME-water-methanol mixture is not an ideal thermodynamic system, requiring the dehydration of methanol to form DME at a temperature of 534 K and a pressure of 0.5 MPa [13].

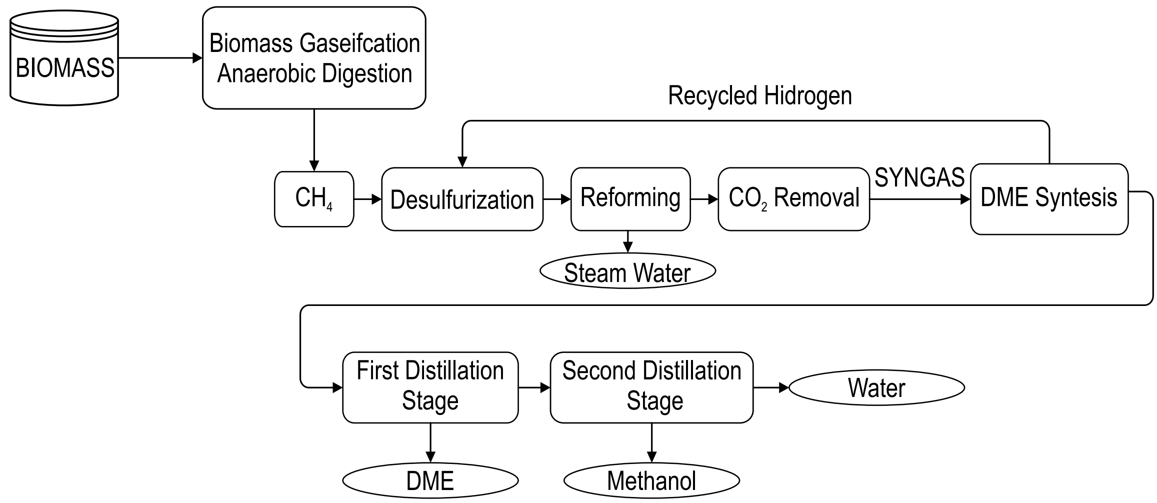
Methanol Dehydration on Solid Acid Catalytic

The indirect production synthesis involves two stages: the DME from biomass-derived synthetic gas undergoes a process using a $Cu/ZnO/Al_2O_3$ catalyst intended for methanol syntheses, and an acid catalyst (usually γ-Al_2O_3) is used for the dehydration of methanol to DME. The author highlights that the synthesis of DME by dehydration requires the conversion of methanol to DME in a fixed bed reactor with copper-based catalysts (Cu/Zn, Cu/3n/Al, Cu/Zn/CO) or solid-acid catalysts [14].

Materials and Methods

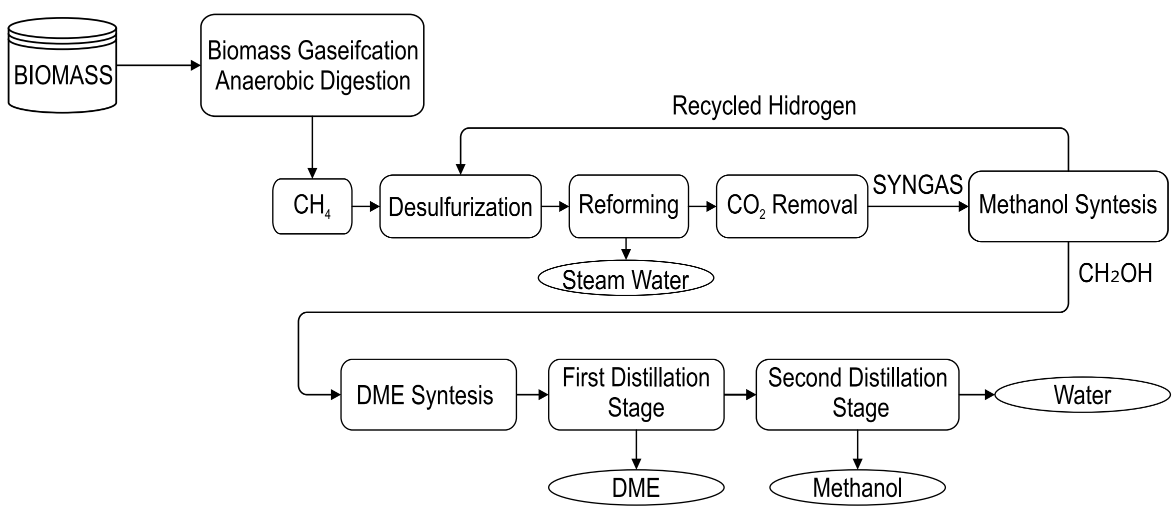
This study used as method the research of DME synthesis processes through a systematic bibliographic review of the production routes: direct

Figure 2. One-step process: Direct method via DME synthesis gas from anaerobic digestion of biomass.



Source: Adapted from Falco (2020) and Wodołażski (2020) [12,13].

Figure 3. Two-stage process: Indirect method via DME synthesis gas from the anaerobic digestion of biomass.



and indirect synthesis, biomethane dehydration, and methanol dehydration in solid acid catalysts resulting from the anaerobic digestion of biomass. The analyses resulted in an analysis of the experimental parameters of the studies presented, focusing on performance, selectivity, and relationship between reagents.

Results and Discussion

Yaripour and colleagues' research on solid-state catalysts for the catalytic dehydration of methane to DME highlights the benefits of a simple metal dehydration method that achieves high conversion rates to DME [15]. His process offers improved selectivity, minimized coke formation, and the option for selective coking using specialized catalysts like DME-AlS. However, it also underscores the importance of biogas pretreatment in two separate stages. Table 1 provides data on reactant generation percentages and catalytic performance, clearly indicating that the silica-modified c- Al_2O_3 catalyst modified with silica has the best performance [15].

Table 1. Methanol dehydration over reference and modified γ-alumina catalysts.

Catalysts Parameters	DME-AlS1	DME-AlS2	DME-AlS3	DME-AlS4	Catalysts	DME-AlS5	DME-SCAT2 (γ- Al_2O_3)
DME (wt%)	75.6	73.4	71.3	64.7	58.6	63.23	73.4
MeOH (wt%)	24.4	26.6	28.7	35.3	41.6	38.77	26.6
CH_4 (wt%)	0.0326	0.0128	–	–	–	–	–
Conversion (X%)	86.4	84.5	85.0	83.5	73.6	77.15	84.5

Source: Adapted from Yaripour and colleagues (2005) [15].

Eichler's study [1] highlights the importance and characteristics of biomass in influencing biomethane levels, which have an average range of 40–70% v/v—lower quality biomass results in a lower biomethane percentage, resulting in lower DME production. Insufficient methanol levels can also lead to reduced efficiency and incomplete inversions. However, biomass pretreatment is necessary to remove impurities and increase the biomethane percentage, which increases operating costs. Direct synthesis of DME from biomass waste using catalysts was analyzed in Liuzzi and Peinaldo study [10], identifying that a high CO_2/CO ratio affects the catalyst performance. The authors suggested that the addition of an aqueous solvent (zeolite 3A) to the reaction process can mitigate the detrimental effect of H_2O in the direct synthesis of DME from CO_2-rich waste, increasing the production of DME through catalysts such as zirconium and gallium.

In another study by Abreu [16], several models of chemical catalysts, several chemical catalyst models were evaluated for experimental settings, finding that the good performance of chemical modeling for biomethane dissolution depends on the experimental points, the conversion rate achieved, and the catalyst acidity. The dissolution of biomethane is crucial for species adsorption models, and constant values for methanol dissolution and water balance are temperature-sensitive.

The data presented in Figure 4 simulates this process using catalysts ZSM-5 and γ-Al2O3 m function of temperature in distinct reactions.

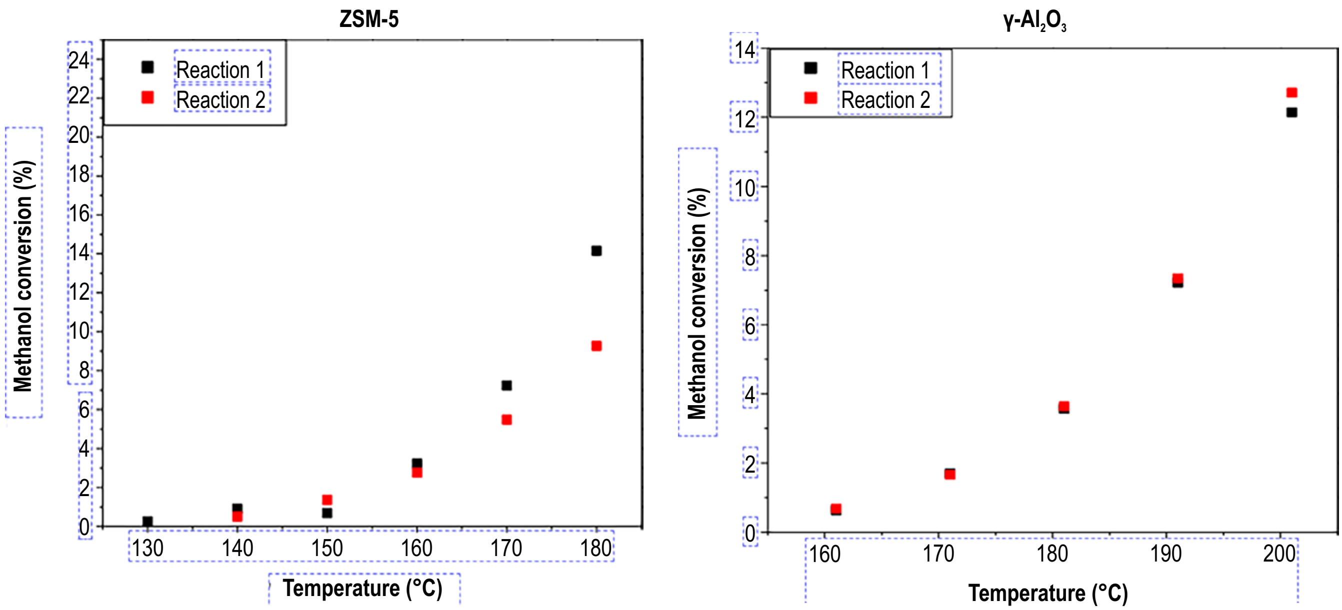
According to the study by Yasar [17], direct synthesis using hybrid catalysts is more advantageous than indirect synthesis, which uses bimetallic or multimetallic catalysts commonly used for biomethane synthesis (Table 2). The biomethane dehydration process utilizes solid catalysts such as Al_2O_3, HZSM-5, SapOS, and SiO_2.

Conclusion

The present work provided a comprehensive review of energy-to-liquid conversion technologies, including the use of DME, highlighting the potential of biomass in the production of aggregate and high-value chemicals and exploring the manufacture of biological-based chemical products from renewable biomass, emphasizing the need for efficient and sustainable conversion processes.

Production of DME can significantly reduce transportation and local labor costs, as well as the use of agro-industrial waste as precursors. DME is a clean alternative to diesel and is suitable for transportation and heating applications. It is a promising fuel and renewable solvent with numerous applications, including clean alternatives to diesel and GLP, offering high ketone numbers and reduced emissions, especially in heavy vehicles. The studies suggest that adding promoters like zirconium oxides and gallium can boost CO in synthesis gas, thereby enhancing DME production rates. Furthermore, adding a water sorbent to the

Figure 4. Conversion in function of temperature using catalyst simulation.



Source: Abreu, (2015) [16].

Table 2. Analysis operating parameters: Production of DME from direct synthesis to derivative of synthesized gas obtained from biomass.

Synthesis	Reactor Type	T (°C)	P(MPa)	Feed Composition/ Space Velocity	Catalysts	(X), (Y), (S)	Authors
Direct	Fixed Bed Reactor	840	2	0.6 kg biomass / h, ER 0.28, CO_2/biomass ratio 0.327	Cu-Zn-Al/ HZSM-5	XCO=2.5 Nm= 78.5% YDME = 379g DME kg^{-1}	Chang (2012)[18]
Direct	Fixed-bed isothermal reactor system	800	2	Raw CO_2 and biomass charcoal. CO_2 / CO =6.33	Ni/Al_2O_3	XCO_2=71.1% XCO=89% YDME=≈65.5 % YCO≈84.8%	Yong (2011) [19]
Direct	Fixed-bed isothermal reactor system	400	3	Similar to biomass-derived synthesis gas CO/CO_2 / H_2 / N_2 = 1/1.9/7.7/1.18	Cu/ZnO/ Al_2O_3 (CZA) Cu/ZnO/ Al_2O_3 (CZA) γ-Al_2O_3	YDME ≈70% XCO and XCO_2 ≈ 7.6 and 9.9%	Dalia and colleagues (2020) [20]
Direct	Fixed bed membrane reactor (PBMR)	240	3	H2/CO = 1 and biomass	Low pressured CZA	BioDME= 49,4% XCO= 96.24% SDME = 70%	FEDELI, (2022) [21]

T, temperature; P, pressure; X, conversion; Y, yeld; S, selectivity.

reaction medium can further boost DME production from CO_2-rich synthesis gas. It can be concluded, according to the analyzed work, that there are critical gaps in the production of DME, noting that industrial processes affect the costs with investment-related expenses (capex), as well as the general operating costs (opex) and that DME synthesis plants can support the current CO_2 capture and seizure plants.

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References

1. Eichler P and colleagues. Bioethanol production via gasification of lignocellulosic biomass. Química Nova 2015;38:10.5935/0100-4042.20150088.
2. Mondal U, Ganapati DY. Perspective of dimethyl ether as fuel: Part I. Catalysis. Journal of CO_2 Utilization 2019;32:299-320.
3. Huang C, Zhu C, Zhang M et al. Design of efficient ZnO/ ZrO_2 modified CuCoAl catalysts for boosting higher alcohol synthesis in syngas conversion. Appl Catal B Environ 2022:300.
4. Turco M, Ausiello A, Micoli L. Processes of Biogas Production: Anaerobic Digestion and Thermal Gasification. In: Treatment of Biogas for Feeding High Temperature Fuel Cells. Green Energy and Technology. Springer, Cham. 2016.
5. Stamatelatou KG, Antonopoulou G. 12-production of biogas via anaerobic digestion. Editor(s): Rafael Luque, Juan Campelo, James Clark. In: Woodhead Publishing. Series in Energy. Handbook of Biofuels Production. Woodhead Publishing, 2011:266-304.
6. Andreides D et al. Biological conversion of carbon monoxide and hydrogen by anaerobic culture: Prospect of anaerobic digestion and thermochemical processes combination. Biotechnology Advances 2022;58:107886.
7. Deka TJ, Osman AI, Baruah DC et al. Methanol fuel production, utilization, and techno-economy: a review. Environ Chem Lett 2022;20:3525–3554.
8. Mota N et al. Direct synthesis of dimethyl ether from CO_2: Recent advances in bifunctional/hybrid catalytic systems. Catalysts 2021;11:411. doi: 10.3390/ CATAL11040411.
9. Peral EMM. Optimal production of dimethyl ether from switchgrass-based syngas via direct synthesis. Industrial & Engineering Chemistry Research. American Chemical Society 2015;54:7465-7475. doi: 10.1021/acs.iecr.5b00823.
10. Liuzzi D, Peinado MA, Peña J et al. Increasing dimethyl ether production from biomass-derived syngas via sorption enhanced dimethyl ether synthesis. Sustainable Energy and Fuels 2020;4:5674-5681. Doi: 10.1039/ D0SE01172J.
11. Aristide G, Catizzone E, Freda C. Process Simulation and environmental aspects of dimethyl ether production from digestate-derived syngas. International Journal of Environmental Research and Public Health 2021;18:807. doi: 10.3390/IJERPH18020807.
12. de Falco M. Dimethyl Ether (DME) Production. In: Oil e Gas Portal, 23 December 2015, Available at: https://www.oil-gasportal.com/ dimethyl-ether-dme-production-2/?print=pdf. 2015.
13. Wodolazski A, Smoliński A. Modeling and process integration study of dimethyl ether synthesis from syngas derived from biomass gasification: Flowsheet simulation. Alexandria Engineering Journal 2020.59:4441-4448.
14. Rafiee A. Staging of diethyl ether (DME) synthesis reactor from synthesis gas (syngas): Direct *versus* indirect route. Chemical Engineering Research and Design 2020;163:157-168. https://doi.org/10.1016/j.cherd.2020.08.033.
15. Yaripour F, Baghaei F, Schmidt I, Perregaard Jens. Catalytic dehydration of methanol to dimethyl ether (DME) over solid-acid catalysts. Catalysis Communications. 2005;6:147-152. 10.1016/j.catcom.2004.11.012.
16. Abreu BMNB. Kinetic modeling of the dehydration of methanol to dimethyl ether. 2015. 107 p.: il. Dissertation.