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Jan F.M. Van Impe, Grégoire Léonard, Satyajeet S. Bhonsale, Monika E. Polańska, Filip Logist (Eds.)

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Valorization of refinery fuel gas and biogenic gases from thermochemical conversion into low-carbon methanol

Eliana Lozano Sanchez[a]*, Erik Lopez-Basto[b,c], and Andrea Ramirez Ramirez [d]

[a] Department of Energy, Aalborg University, Aalborg, Denmark
[b] Cartagena Refinery. Ecopetrol S.A., Colombia
[c] Department of Engineering Systems and Services, Faculty of Technology, Policy and Management, Delft University of Technology, Delft, The Netherlands
[d] Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Delft, The Netherlands
* Corresponding author: els@energy.aau.dk.

ABSTRACT

By-product fuel gases from refinery operations are a major heat source in fossil refineries and their availability poses a challenge to the deployment of low-carbon heat sources. This study evaluates the valorization of refinery fuel gases (RFG) into low-carbon methanol via co-processing with residual biogenic gas streams from biomass thermochemical conversion. Results from techno-economic analysis indicate that up to 44 wt.% of biogenic blend is possible without the need for external hydrogen supply, while electricity and heat requirements per tonne of methanol change by -4 % and + 80% respectively. Nevertheless, at the 44 wt.% blend, the estimated methanol cost increases only by 2.4 % (0.43 EUR/kg), while the reduction in methanol carbon intensity is approximately 40 %. This highlights promising benefits that can contribute to the integration of bio-oils producing technologies within fossil refineries.

Keywords: Technoeconomic Analysis, Biomass, Refining, Biofuels, Process Design.

INTRODUCTION

Heat decarbonization is a major strategy for fossil refineries to achieve emission reductions in the short/medium term. Direct electrification and other low carbon heat sources are expected to play a key role, however, availability of surplus refinery fuel gases (RFG) – a mixture of residual gases rich in hydrocarbons used for on-site heat generation - may limit decarbonization efforts if alternative uses for surplus RFG are not explored.

Excessive production of RFG and the challenge it brings for the implementation of energy reduction projects in refineries is not a new topic. Over the years, increasing emphasis on higher energy efficiency and lower emissions has resulted in less fuel consumption, making energy reduction projects less attractive in cases where these could result in flaring the RFG produced [1]. Some options discussed in literature to reduce RFG disposition are to increase hydrogen recovery in PSA/membrane units, improve liquid recovery in separators to reduce C_{3+} components in the gas, optimize fuel system control to minimize fuel imports, or include co-generation units that use RFG to produce additional heat and power [1–3]. Nevertheless, there is a lack of studies that explore further utilization options, particularly in the context of the integration of biomass technologies that represent a valuable source of renewable carbon for refineries.

In recent years, there has been increasing interest in biomass thermochemical conversion technologies and particularly in bio-oil producing technologies such as fast pyrolysis (FP) and hydrothermal liquefaction (HTL) due to their potential to deliver drop-in biofuels that can be integrated within existing refinery infrastructure. Although co-processing of bio-oils has been extensively discussed in literature [4–6], there is a lack of studies that explore the integration of by-products within a refinery context to increase biogenic carbon conversion into valuable products.

This study presents a techno-economic assessment of co-processing by-product gases from biomass thermochemical conversion with RFG to produce methanol, a key chemical with high demand in industry and as shipping fuel. The impact of co-feeding HTL gas or FP gas with RFG is evaluated in terms of overall carbon efficiency to methanol, energy requirements, methanol production cost and carbon intensity.

METHODS

Process description

A simplified process flow diagram of the system evaluated is presented in Figure 1. A mixture of surplus RFG and HTL or FP gas is converted into methanol following a two-step process: steam reforming to produce syngas and methanol synthesis via CO_2/CO hydrogenation. The RFG and HTL/FP gases are by-products of the refinery and biomass thermochemical conversion processes, respectively and are the starting point of this analysis.

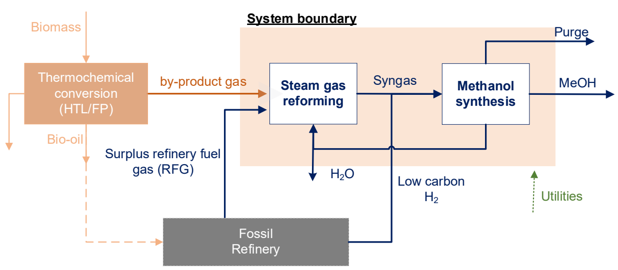

Figure 1. Simplified diagram of integrated biomass liquefaction in refinery context with co-processing of by-product gases for methanol synthesis.

Table 1: Composition of refinery fuel gas (RFG) and by-product gases from hydrothermal liquefaction (HTL) and fast pyrolysis (FP) of forestry residues (dry basis).

	RFG	**HTL gas**	**FP gas**
Temperature [C]	40	30	30
Pressure [bar a]	5.15	1	1
Composition [mol%]			
CO_2	1.50	90.20	34.72
Hydrogen	38.22	0.90	0.00
CO	2.21	0.00	45.94
Methane	33.85	3.00	12.82
Ethane	16.44	2.50	1.50
Ethylene	0.00	0.00	5.02
C_3	2.18	1.90	-
C_4	2.23	1.50	-
C_{5+}	1.78	-	-
H_2S	1.59	-	-
LHVstd [MJ/kg]	46.96*	3.30*	9.99*

The process is modelled in Aspen HYSYS V12.1 assuming a fixed RFG input of 25 tonne/h, which corresponds to an estimated RFG surplus in a refinery case study after initial emission reduction measures. The impact of gas co-processing is evaluated for increasing ratios of HTL gas or FP gas blended with RFG, from 0% (RFG case) to 100% (full biogenic carbon case), in terms of hydrogen requirement, carbon conversion to methanol, overall water balance and energy consumption. The analysis is performed for the HTL gas and FP gas separately. The composition of the input gas streams is presented in Table 1. The main process steps are briefly described in the following sections.

Steam gas reforming (SMR)

The feed gases are pressurized to 30 bar, mixed with steam (steam/carbon ratio S/C= 4), pre-heated to 400 ℃ to enter the pre-reformer, and sent to the main steam reformer at 900℃. In the pre-reformer, conversion of C_{2+} hydrocarbons to methane and hydrogen is favored at relatively lower temperatures, while endothermic steam reforming reactions are favored at higher temperatures in the main reformer. The produced syngas is cooled down to 30 ℃ to condense water that is reused for steam generation. The reformer is simulated as a furnace and a Gibbs reactor, so the heat requirement is the sum of the furnace duty and the reaction heat at 900 ℃. This configuration allows heat integration between the flue gases, reformer products and feeds, including the furnace fuel (CH_4) and air, resembling typical SMR configurations. Removal of H_2S upstream the reactor is required to avoid catalyst poisoning and it is implemented for the RFG via caustic wash with NaOH; however, this step is not included for the HTL/FP gases since H_2S was not reported in the data consulted [8].

Methanol synthesis

Methanol is produced via catalytic hydrogenation of CO_2 and CO, in which a minimum ratio between hydrogen and carbon oxides is required (stoichiometric number, $SN=H_2\text{-}CO_2/CO_2+CO=2$). After reforming, the SN of the syngas is calculated and, if required, hydrogen is added to satisfy the minimum SN. The adjusted syngas is pressurized to 60 bar and preheated to 220̊ C to enter the methanol synthesis reactor (Gibbs reactor) in which a reaction temperature of 250 ℃ is specified based on [7]. The reactor products are cooled down to 30 ℃ and separated at high pressure, with the unreacted gases being recirculated and the liquid products sent to distillation to obtain high purity methanol. A purge of 3% is included to avoid accumulation of inerts (unconverted hydrocarbons) in the system, and its potential use as fuel in the reformer furnace is evaluated (85 % furnace efficiency). Water obtained as by-product (99.9 mol%) is recirculated to the reforming process to decrease external water consumption for steam generation.

Economic evaluation

An economic evaluation is conducted to assess the impact of co-processing in the methanol minimum selling price at increasing HTL/FP gas ratios. Capital and operational expenses are estimated using the cost parameters in Table 2. In terms of Capex, purchase equipment costs of the SMR (including the heat supply system) and methanol production process reported in literature with reference year 2020 are adjusted to 2021 euros (EUR) and scaled to the required size using the CEPCI index and a scaling factor of 0.7. Fixed (FCI) and total capital investment (TCI) are estimated from the total purchase equipment costs (TPE) multiplied by a factor of 4.8 and 5.8 respectively [9]. In terms of feedstock, there is no reported selling price of RFG, HTL or FP gases since these are not traded as products but used (or expected to be used) for heat purposes. Consequently, their price is assumed to be proportional to the price of methane times the LHV ratio. Operation and maintenance (O&M) and other fixed costs (local taxes, insurance, plant overhead and administrative costs) are estimated based on detailed methodology in literature [10]. The methanol price is then estimated using a net present value (NPV) analysis with a 10% discount rate, straight line depreciation and a plant lifetime of 25 years.

Table 2: Cost parameters and assumptions used in the economic evaluation.

	Base case	Low case	High case
Equipment cost			
SMR [$MEUR_{2020}$] [11] (kt/d feed [a])	24.5 (9.9)	--	--
MeOH synthesis [$MEUR_{2020}$] [12] (kt/d MeOH)	15.7 (0.3)	--	--
Variable costs			
Natural gas (NG) price [EUR/GJ] [13]	6.63	5.43	7.54
RFG price [b] [EUR/GJ]	6.23	5.10	7.08
HTL gas price [b] [EUR/GJ]	0.44	0.36	0.50
FP gas price [b] [EUR/GJ]	1.33	1.09	1.51
Low carbon H_2 price [EUR/kg]	2.50 [c]	2.20 [d]	4.60 [e]
Electricity price [EUR/MWh] [f]	60.00	40.00	68.00
Demineralized water price [EUR/m^3]	0.51	--	--
Cooling water price [EUR/m^3]	0.42	--	--
Other parameters			
Scaling factor	0.70	--	--
Hourly labor cost	31.40	--	--
Operators per shift	6	--	--
Furnace efficiency	0.85	--	--
Annual operation hours	8000	--	--

a. SMR including heat supply system, scaled based on total feed mass flow (steam + natural gas).
b. Price estimated based on the gas calorific value relative to natural gas ($LHV_{gas}/LHV_{NG} * NG_{price}$).
c. Blue H_2 (NG SMR with carbon capture) based on natural gas price of 5.4 EUR/GJ [13].
d. Produced via electrolysis based on an electricity consumption of 53 kWh/kg H2 and capex of 315 EUR/kW [13]
e. Produced via electrolysis based on an electricity consumption of 59 kWh/kg H2 and capex of 575 EUR/kW [13]
f. Price range in line with wholesale electricity prices reported in Denmark and The Netherlands in 2021 [16]

Carbon intensity of methanol

The impact of co-processing biogenic streams in the methanol carbon intensity is evaluated based on the main scope 1 emission reported in Table 3. CO_2 emissions from the RFG are calculated based on the carbon content, while no CO_2 equivalent is allocated to the HTL/FP gases. This assumption is considered reasonable since these are by-products of the bio-oil production process with very low energetic or economic value and would only yield biogenic CO_2 if they were to be used for heat purposes in the upstream process. Regarding the electricity and H_2 contributions, low and high emission scenarios are considered due to the well-known impact of the hydrogen source in the carbon intensity of synthetic fuels. An electricity carbon intensity between 50 and 250 kg CO_2eq/MWh is considered based on 2023 data for European countries such as France, Denmark and Netherlands [14]. Natural gas is assumed as make-up heating source, but up-stream leakage is not included in the analysis. The methanol carbon intensity is then estimated as the sum of the listed contributions for 0% to 100% biogenic blends with RFG.

Table 3: Scope 1 emission sources included in methanol carbon intensity estimation.

Emission source	Base case	Low case	High case
Refinery fuel gas (RFG) [kg CO_2eq/h]	65.48	65.48	65.48
HTL/FP gas [kg CO_2eq/h]	0.00	0.00	0.00
Heating (Natural gas) [kg CO_2eq/MWh]	15.58	15.58	15.58
Electricity [kg CO_2eq/MWh]	150.00	50.00	250.00
Low carbon H_2 [kg CO_2eq/kg H_2]	3.00[a]	2.65[b]	3.38[c]

a. Defined in EU taxonomy based on GHG emission savings of 73.4% in comparison to the fossil fuel comparator of 94 g CO_2eq/MJ (https://ec.europa.eu/sustainable-finance-taxonomy/faq).
b. Calculated for electrolytic hydrogen based on an electricity consumption of 53 kWh/kg H_2 and carbon intensity of 50 kg CO_2eq/MWh.
c. Threshold in RFNBO regulation of 70 % reduction relative to fossil comparator of 94 g CO_2eq/MJ.

RESULTS

Impact of co-processing in mass balance

Figure 2 shows the distribution of reactants and products for increasing shares of HTL gas in the feed (see results of the FP gas case in the supplementary material). Regarding the reactants, there is a steady decrease in water consumption due to a combined effect of less hydrocarbons in the feed gas that reduce the steam input for SMR, plus increased water production from the methanol synthesis that gets recirculated. The reduction in the hydrocarbons content results in less H_2 in the syngas until SN=2 at 42.8 wt% blend, above which make-up

H_2 is required. This condition is met at a 44 wt% blend with FP gas due to its higher hydrocarbon content, however, for simplicity, the neutral-H_2 blend used for both cases is 44% in the rest of the discussion.

In terms of products, methanol production drops at increasing HTL gas shares, going from 41.2 t/h in the RFG case to 18.9 t/h in the HTL gas case (23.8 t/h for FP). This is a direct result of less carbon in the gas blend by increasing the CO_2 content. Although the carbon conversion is estimated between 84 and 90%, future studies including reaction kinetics are recommended for a more detailed assessment of the impact in conversion.

Figure 3 shows the overall mass balance for the H_2 neutral blend of 42.8 % HTL gas. Despite of not being within scope of the present study, the indirect biomass consumption for bio-oil production in the HTL process is estimated in 1.5 kt/d, being in the range of relatively large biomass conversion plants (2.2 kt/d in the FP gas). More detailed information on streams composition and process conditions can be found in the supplementary material.

Impact of co-processing in energy needs

Electricity and heat requirements are summarized in Table 4 for 0%, 44 % and 100 % HTL gas blend with RFG. Overall, the total electricity use in the 44% case is the lowest evaluated due to a lower syngas flow, absence of external hydrogen, and thus less work required for compression (see details in supplementary material). Nevertheless, the specific electricity consumption is approximately the same as in the RFG case (0.2 MWh/t MeOH) due to the lower methanol production. The full biogenic cases exhibit much higher specific electricity consumption (0.44 and 0.39 MWh/t MeOH respectively) despite having about the same total requirement as the RFG case due to reduced methanol throughput.

Table 4: Energy consumption in 0%, 44 % and 100 % HTL gas blend with RFG.

	0 %	44 %	100 %
Heat [MW]			
Total heat requirement	135.2	87.7	27.5
Heat potential vent (LHV)	111.1	35.3	12.3
Net Heat requirement	40.8	57.7	17.1
Specific heat [MWh/t MeOH]	1.0	1.9	0.9
Electricity [MW]			
Total electricity requirement	8.2	5.6	8.3
Specific electricity [kWh/t MeOH]	198.3	189.3	440.9

In terms of heat, the total demand decreases with increasing biogenic gas share due to less steam needed to maintain the same SMR S/C ratio. For all three cases, the unconverted gases have potential to reduce the SMR fuel input significantly; however, the specific heat required is substantial, being almost twice in the 44% blend (+82.8 % in the FP blend). Process modifications such as electrified SMR [15] or advanced distillation concepts for methanol production [7] are recommended in future studies to lower the heat requirement.

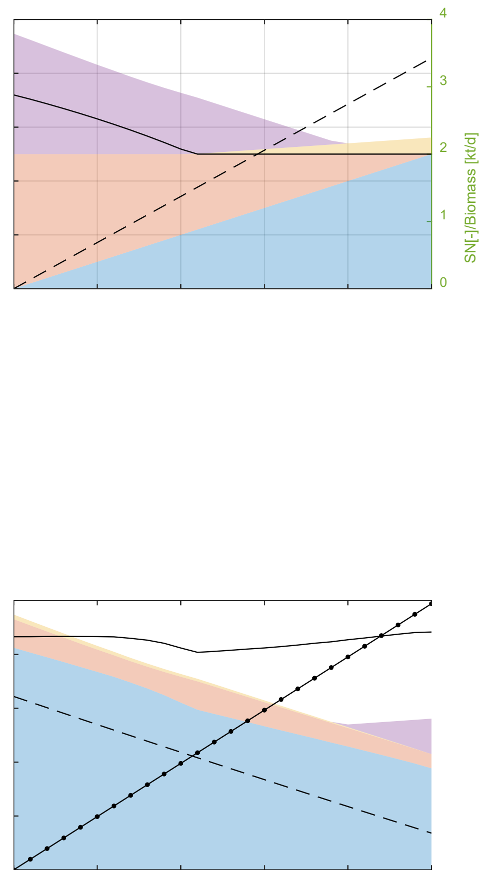

Figure 2. Change in mass flows with increasing share of HTL gas in blend with RFG (% in mass basis).

Methanol production costs and carbon intensity

The results in Figure 4 show the trade-off between methanol cost and carbon intensity at increasing ratios of the biogenic carbon feeds. Co-processing of HTL gas increases the methanol production cost from 0.42 EUR/kg to 0.71 EUR/kg in the full HTL gas case. However, as observed in the plot, the increase is only marginal until 44% blend (+2.4 %) and becomes significant from this point onwards due to the growing H_2 requirement. The FP gas case shows the same trend, but the increase in cost is

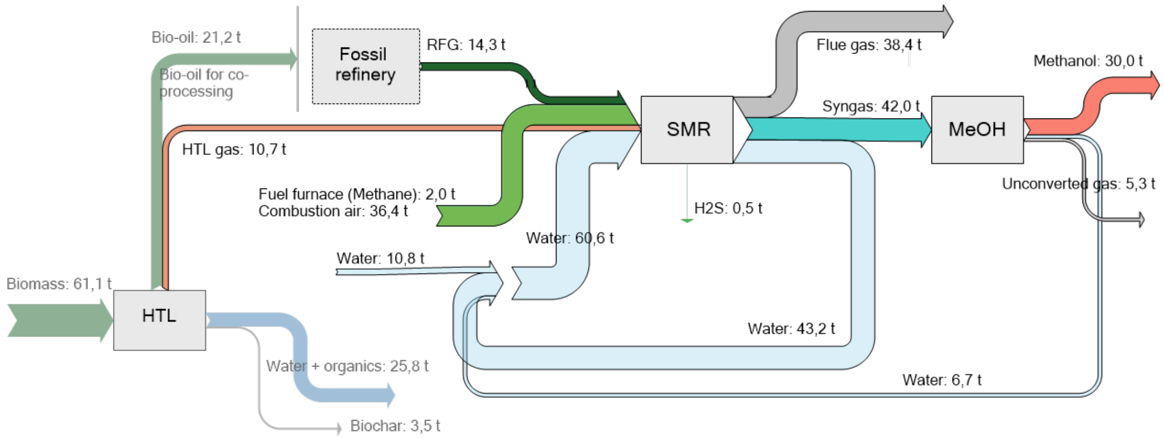

Figure 3. Mass Sankey diagram of HTL gas co-process with RFG (42.8 % case).

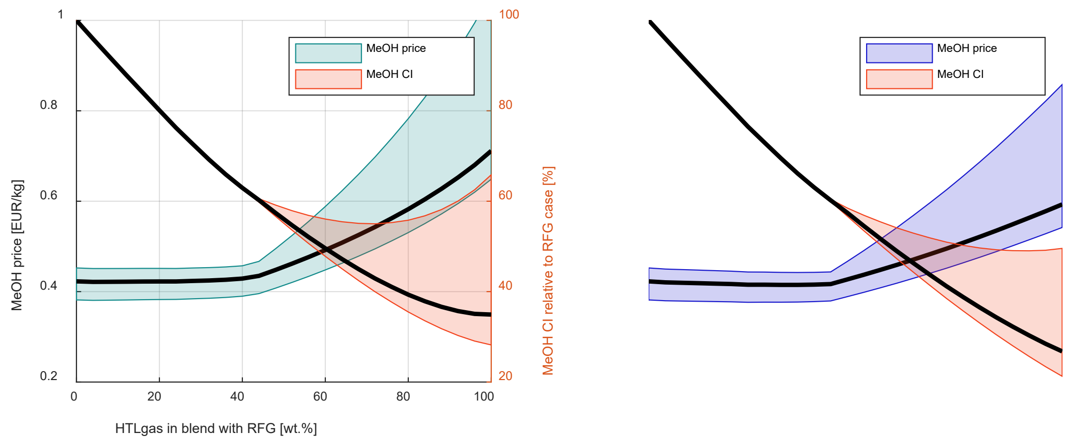

Figure 4. Mass Sankey diagram of HTL gas co-process with RFG (42.8 % case).

lower than for HTL due to slightly lower hydrogen needs and higher methanol production.

In the full biogenic feed cases, the estimated methanol carbon intensity is 27 and 36 kg CO_2eq/GJ, being in the range of the 65 % GHG reduction target by the REDIII relative to the fossil comparator (35.6 kg CO_2eq/GJ methanol). In these results, H_2 has by far the largest carbon footprint contribution followed by the electricity, causing variations in the estimated carbon intensity between -5% and + 30 % in the low and high scenarios considered. These could result in even higher emissions of the full biogenic case compared to the co-processing route, represented by the shadow areas in Figure 6. Lower variations in price and carbon footprint are observed up to the 44% blend since the H_2 impact is avoided. A life-cycle assessment of the integrated system is recommended in future studies for a more detailed evaluation of environmental impacts.

CONCLUSIONS

- Co-processing by-product gases from thermochemical biomass conversion is deemed as a favorable strategy to valorize surplus RFG into low-carbon methanol, adding to the potential benefits of integrating bio-oil producing technologies within oil refineries.
- Co-processing 44% biogenic gas is identified as a suitable strategy that avoids the need of external H_2 supply. At this point, the estimated methanol cost is only 2.4 % higher than the RFG reference (0.43 EUR/kg), while the reduction in carbon intensity is approximately 40 %.
- The main impact of co-processing rich CO_2 streams with RFG is the reduction in methanol throughput. Although this increases the specific heat consumption (+89.5 %), the methanol cost is not affected significantly and the increased share of biogenic carbon in the product has a dominant positive impact.
- Detailed kinetics and LCA studies are recommended in the future to address the limitations of this study and further improve the analysis.

DIGITAL SUPPLEMENTARY MATERIAL

The supplementary material can be consulted in http://PSEcommunity.org/LAPSE:2025.0014.

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REFERENCES

1. Rossiter, A. P. & Jones, B. P. Energy Management and Efficiency for the Process Industries. (John Wiley & Sons, Inc., Hoboken, New Jersey, 2015). doi:10.1002/9781119033226.
2. Nazerifard, R., Mohammadpourfard, M. & Zeinali Heris, S. Design, thermodynamic and economic evaluation, and optimization of gasoline production from refinery furnaces flue gas. Energy Convers Manag 293, 117492 (2023).
3. Zhou, L. et al. Energy configuration and operation optimization of refinery fuel gas networks. Appl Energy 139, 365–375 (2015).
4. Lindfors, C., Elliott, D. C., Prins, W., Oasmaa, A. & Lehtonen, J. Co-processing of Biocrudes in Oil Refineries. Energy & Fuels 37, 799–804 (2023).
5. Sharma, K., Pedersen, T. H., Toor, S. S., Schuurman, Y. & Rosendahl, L. A. Detailed Investigation of Compatibility of Hydrothermal Liquefaction Derived Biocrude Oil with Fossil Fuel for Corefining to Drop-in Biofuels through Structural and Compositional Analysis. ACS Sustain Chem Eng 8, 8111–8123 (2020).
6. van Dyk, S., Su, J., Mcmillan, J. D. & Saddler, J. (John). Potential synergies of drop-in biofuel production with further co-processing at oil refineries. Biofuels, Bioproducts and Biorefining 13, 760–775 (2019).
7. Vaquerizo, L. & Kiss, A. A. Thermally self-sufficient process for cleaner production of e-methanol by CO2 hydrogenation. J Clean Prod 433, 139845 (2023).
8. Tews, I. J. et al. Biomass Direct Liquefaction Options. TechnoEconomic and Life Cycle Assessment. https://www.osti.gov/biblio/1184983 (2014) doi:10.2172/1184983.
9. Seider, W. D., Seader, J. D. & Lewin, D. R. Product and Process Design Principles: Synthesis, Analysis, and Evaluation. (Wiley, 2004).
10. de Jong, S. et al. Cost optimization of biofuel production – The impact of scale, integration, transport and supply chain configurations. Appl Energy 195, 1055–1070 (2017).
11. Oni, A. O., Anaya, K., Giwa, T., Di Lullo, G. & Kumar, A. Comparative assessment of blue hydrogen from steam methane reforming, autothermal reforming, and natural gas decomposition technologies for natural gas-producing regions. Energy Convers Manag 254, 115245 (2022).
12. Vaquerizo, L. & Kiss, A. A. Thermally self-sufficient process for cleaner production of e-methanol by CO2 hydrogenation. J Clean Prod 433, 139845 (2023).
13. López-Basto, E., Korevaar, G., Tanzer, S. E. & Ramírez, A. R. Assessing the impacts of low-carbon intensity hydrogen integration in oil refineries. Cleaner Energy Systems 9, 100161 (2024).
14. Statista. Carbon intensity of the power sector in the European Union in 2023, by country. https://www.statista.com/statistics/1291750/carbon-intensity-power-sector-eu-country/#:~:text=Power%20sector%20carbon%20intensity%20in%20the%20European%20Union%202023%2C%20by%20country&text=Poland's%20power%20sector%20had%20the,just%20over%20530%20gCO%E2%82%82%2FkWh. (2024).
15. From, T. N. et al. Electrified steam methane reforming of biogas for sustainable syngas manufacturing and next-generation of plant design: A pilot plant study. Chemical Engineering Journal 479, 147205 (2024).
16. EMBER. https://ember-energy.org/data/european-electricity-prices-and-costs/