CHEMICAL ENGINEERING TRANSACTIONS

VOL. 114, 2024

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Min Zeng, Yee Van Fan, Xuechao Wang

ISBN 979-12-81206-12-0; **ISSN** 2283-9216

DOI: 10.3303/CET24114083

Process Reconfiguration for the Production of 1, 4-Butanediol Integrating Coal with Off-grid Renewable Electricity

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1,4-Butanediol (BDO), an important organic chemical material, is primarily produced through the Reppe process. The process is known for being an industry with high energy consumption and pollution levels. A novel reconfiguration process coupled with renewable energy is proposed in this paper based on the analysis of the conventional coal-to-1,4-butanediol (CtBDO) process. A new calcium carbide production process, the Coal-Coke-Electricity Grading Substitution Method (GSM), and the coal-to-methanol (CtM) process with near-zero carbon emissions, the pulverized coal gasification integrated green hydrogen (PCGwGH-CtM) system, are introduced. Moreover, electrification is utilized to decrease indirect carbon dioxide emissions. The techno-environmental-economic evaluation of the reconfigured BDO production process is being analyzed. The results show that the carbon utilization rate increased from 34.03 % to 67.75 %. the direct CO_2 emission intensity is reduced from 3,847 kg/t BDO and 837 kg/t BDO compared with the conventional process, and the indirect CO_2 emission intensity is reduced from 1,824 kg/t BDO to 379 kg/t BDO. Energy efficiency is increased from 40.17 % and 43.28 %. Through economic analysis, the production cost of conventional and reconfiguration processes is 9,869 CNY·t^{-1}BDO and 14,467 CNY·t^{-1}BDO, respectively. When the renewable energy drops to 0.2 CNY·kWh^{-1}, the reconfiguration process becomes economically feasible. This study provides an important reference for the CtBDO-coupled renewable energy and helps to promote sustainable development in the industry.

1. Introduction

Nowadays, the widespread misuse of traditional plastics significantly contributes to severe plastic pollution on Earth (Zhao et al., 2024). The use of biodegradable plastics, such as PBAT (polybutylene adipate/terephthalate), PBS (polybutylene succinate), PLA (polylactic acid), and PHA (polyhydroxyalkanoates), has been proven to be one of the promising approaches to mitigate adverse environmental impacts (Vollmer et al., 2020). BDO is one of the primary precursor materials to produce PBS and PBAT (Xu et al., 2023). The Reppe method is the most widely used technique for synthesizing BDO, constituting approximately 75 % of China's total capacity by 2019 (Luo and Li, 2021). The Reppe method consists of two steps: (1) formaldehyde (FA) and acetylene (C_2H_2) react to synthesize 1,4-butynediol (BYD), and then (2) BYD is hydrogenated to BDO. In China, the primary source of upstream raw materials for the production of FA, C_2H_2, and H_2 production predominantly stems from coal.

The process of using coal as raw material is often accompanied by serious environmental problems, but many researchers have proposed improvement measures for this problem. The industrial production method of formaldehyde mainly relies on methanol oxidation. Nowadays, over 77 % of methanol is produced using the coal-to-methanol technique. It is reported that the carbon dioxide emission intensity of CTM process is 2.66–3.56 t CO_2/t MeOH. Wang et al. (2022) has proposed the novel process with near-zero carbon emission, pulverized coal gasification integrated green hydrogen (PCGwGH-CTM) system. As an indispensable raw material for BDO, the key step in the coal-to-acetylene process is the production of calcium carbide (CaC_2). At present, the electro-thermal calcium carbide manufacturing (ETM) process is the dominant method for producing CaC_2. The CaC_2 requires 3,500 kW·h of electricity per ton of CaC_2 and results in the emission of 400 cubic meters of off-gas containing a high concentration of carbon monoxide (CO). Ma et al. (2022) has proposed a new calcium carbide production process of coal-coke-electricity grading substitution method (GSM). The H_2 production involves coal-based syngas through the water gas shift (WGS) and purification processes. Although

Paper Received: 2 May 2024; Revised: 4 September 2024; Accepted: 2 December 2024
Please cite this article as: Wang D., Li Y., 2024, Process Reconfiguration for the Production of 1, 4-Butanediol Integrating Coal with Off-grid Renewable Electricity, Chemical Engineering Transactions, 114, 493-498 DOI:10.3303/CET24114083

this approach is well-established and extensive, it has numerous drawbacks, such as high energy consumption and elevated carbon emissions, which do not align with the low-carbon development needs of the hydrogen industry in the future. In contrast, water electrolysis for H_2 production driven by renewable energy is considered one of the cleanest and most environmentally friendly technologies. Alkaline water electrolyzers (ALK) are commonly used to produce hydrogen in large-scale applications. The share of indirect carbon emissions will be higher due to the heavy reliance on coal. To solve this problem, consensus is growing that electrification may be required to meet GHG reduction goals (Chen et al., 2019). Solar and wind power could be exploited to provide the required duties in terms of heat and electricity to industrial processes that are conventionally fed by energy deriving from fossil fuels such as methane or oil combustion to provide thermal duties (Alessandro Di Pretoroa et al., 2023).
At present, the research on the synthesis process of BDO is mostly focused on the reaction section, and its harm to the environment is rarely analyzed from the raw material preparation stage. Therefore, this paper proposes a reconfiguration process to reduce carbon emissions from the source. The characteristics of the novel process have been presented: (a) The AWE hydrogen production process is used as an alternative to the coal-based hydrogen production process. (b) Methanol production by integrating pulverized coal gasification with green hydrogen is utilized as an alternative to the conventional CtM production process. (c) A new calcium carbide production process of coal-coke-electricity grading substitution method is utilized as an alternative to ETM process. (d) The process meets the needs of utility systems through a renewable energy supply. To verify the feasibility of the reconfiguration process, based on the results of Aspen Plus software modeling of each unit, this study compares the technical-environmental-economic performance of the two processes from the aspects of carbon utilization rate, CO_2 emission intensity, energy efficiency and production cost.

2. Process description

2.1 Process description of the CtBDO process

The conventional CtBDO process primarily consists of eight primary processes, serving as the benchmark case, including coal to hydrogen (CtH) process, coal to methanol (CtM) process, formaldehyde synthesis (FS) process, coal coking (CC) process, electro-thermal calcium carbide manufacturing (ETM) process, acetylene synthesis (AS) process, ethynylation of formaldehyde (EF) process, and hydrogenation of BYD (BDO) process.

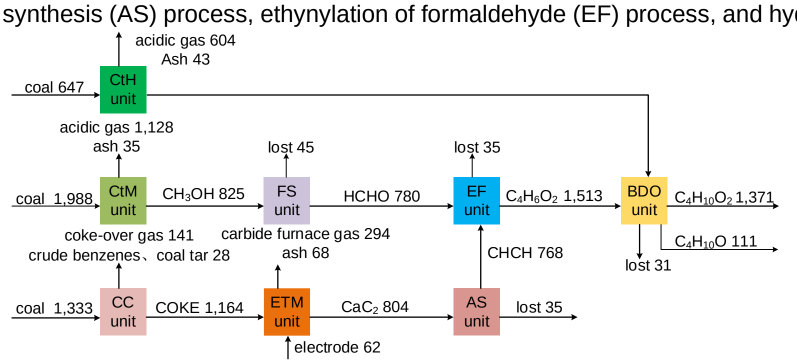

Figure 1 : Schematic representation and Carbon-flow of the CtBDO process, kmol/h

In the CC unit, raw coal undergoes a series of reactions to produce products such as coke and coke-oven gas under conditions of isolated air and high temperature. A portion of the coke-oven gas is mixed with the preheated air in the combustion chamber to provide heat for the carbonization chamber, while the remainder undergoes purification through cooling and desulfurization. The coke is first sent to the coke quenching section and then to the carbide furnace (ETM unit). An electrode heats lime to 2,000 °C, resulting in the production of calcium carbide (CaC_2) and furnace gas. The calcium carbide furnace gas is mainly composed of CO, which can be used to produce steam. Calcium carbide enters the AS unit, reacts with excess water to produce crude acetylene gas and carbide slag. The crude acetylene gas is purified through pickling to remove acid gases and then pressurized and sent to the EF unit. Methanol, produced from coal conversion, is distilled to 99.9 % purity, and then combined with compressed air in the FS unit to create formaldehyde and water. The formaldehyde is sent to the EF unit to react with acetylene to form 1,4-butynediol. Hydrogen, also derived from coal conversion, is directly utilized in the 1,4-butanediol synthesis unit to convert 1,4-butynediol through a hydrogenation process. It is important to note that in the methanol and hydrogen synthesis stages, some CO in the syngas reacts with water in the water-gas-shift unit to produce H_2 and CO_2, leading to significant CO_2 emissions and carbon wastage. The conventional process diagram and the carbon flow diagram, based on the molar flow conversion of carbon atoms contained in each substance in the material balance results, are shown in Figure.1. In the CC unit, CtH unit, CtM unit, and ETM unit, the carbon loss is up to 169 kmol/h, 647 kmol/h, 1,163 kmol/h, and 362 kmol/h.

2.2 Reconfiguration process

By analyzing the conventional CtBDO process, the primary source of carbon emissions in the BDO production process is the upstream raw materials used to produce FA, C_2H_2, and H_2. This paper proposes a process reconfiguration for producing 1,4-butanediol by integrating the AWE hydrogen production process, coal-to-methanol process coupled with green hydrogen, and calcium carbide production process using coal-coke-electricity grading substitution method. The computational benchmark for process modeling is to ensure a consistent yield of BDO.
The proposed modified CtBDO process is referred to as the AWE-CtBDO process, which includes the AWE process, PCGwGH-CtM process, GSM process, FS process, AS process, EF process, and BDO process. A new calcium carbide production process, known as the coal-coke-electricity grading substitution method, can be viewed as an improved electro-thermal system for preparing calcium carbide. It comprises a pyrolysis furnace and a calcium carbide furnace. Pellets fully mixed with pulverized coal and quicklime powder under a certain pressure are used as raw materials to enter the pyrolysis furnace. They are heated to a pyrolysis temperature of 800 °C, during which the coal decomposes into coke, pyrolysis furnace gas, tar, and water. Then the pyrolyzed hot pellets enter the calcium carbide furnace. The coke undergoes a reaction with quicklime within a temperature range of 1,600 °C to 2,000 °C in the calcium carbide furnace. The pyrolysis furnace gas contains a high concentration of H_2. Part of the pyrolysis furnace gas returns to the furnace for combustion to provide energy for the pyrolysis process, while another part could be utilized for hydrogen recovery. The calcium carbide tail gas, which is abundant in CO, is pressurized and purified before being sent to the PCGwGH-CtM process for methanol synthesis. The PCGwGH-CtM process introduces green hydrogen to meet the H/C ratio, avoids the AS unit that consumes a large amount of energy, eliminates the water-gas-shift unit that produces a large amount of CO_2, and utilizes a simplified acid gas removal process to remove H_2S in the crude syngas. Water electrolysis offers advantages over other traditional hydrogen generation technologies that rely on fossil fuels because it produces minimal carbon emissions when combined with a renewable energy source. The advantages of alkaline electrolyzers are that they can operate at low temperatures and do not require catalysts to activate and produce hydrogen. The configuration of the other four units is consistent with the conventional CtBDO process. The schematic representation and carbon flow diagram of the reconfiguration process are shown in Figure.2.

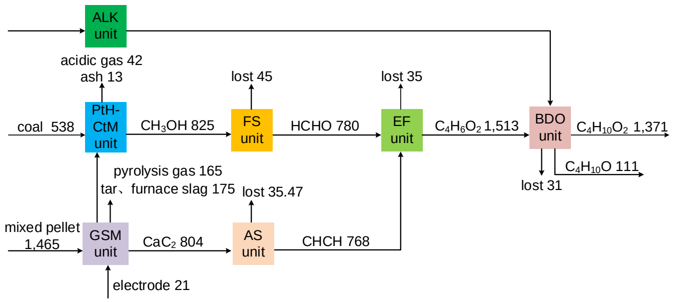

Figure 2: Schematic representation and Carbon-flow of the ALK-CtBDO process, kmol/h

3. Results and discussion

Modeling of the CtBDO and ALK-CtBDO is performed using Aspen Plus software. The BDO model is established based on a yearly production time of 8000 hours and a BDO production rate of 30.99 t/h. Subsequent to the process modeling outcomes, technical and economic evaluations are carried out.

3.1 Carbon utilization efficiency

Carbon utilization efficiency is a measure of the extent of carbon conversion used to assess the utilization of carbon atoms. It is defined as the carbon molar flow in the production of 1,4-butanediol divided by the carbon molar flow in the raw coal. The calculation formula is as follows:

$$\alpha = \frac{M_{BDO}^{out} + M_{NBA}^{out}}{M_{Coal}^{in}} \quad (1)$$

Where α denotes the carbon utilization efficiency, and M denotes the carbon molar flow in BDO, n-butanol (NBA) and raw coal, respectively.
The carbon utilization rate of the conventional process is only 34.03 %. Compared with the conventional process that completely relies on coal as raw material, the reconfiguration process effectively improves the utilization rate of carbon element, which has increased to 67.75 %.

3.2 Carbon emissions

In this paper, it is assumed that the lost carbon is consumed in the form of CO_2, so as to calculate the direct carbon emission. In order to facilitate the analysis, the CC and ETM units of the conventional process, as a whole, are compared with the GSM unit. According to the Figure.3a, the direct CO_2 emissions for the conventional process are 3,847 kg/t BDO, whereas in the reconfiguration process, they are 837 kg/t BDO.

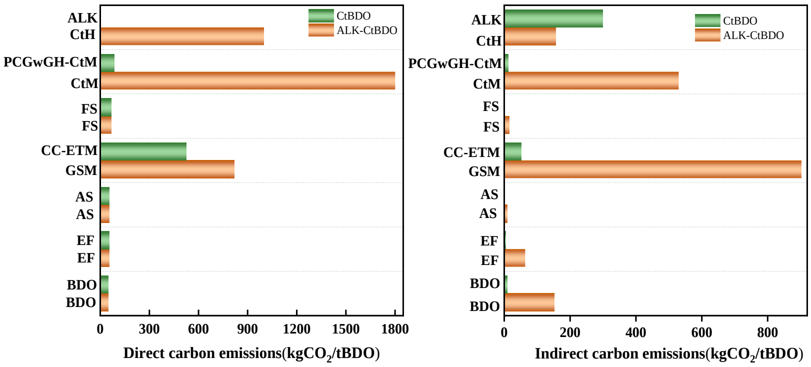

Figure 3: Direct and indirect emissions of carbon in each unit of the CtBDO and ALK-CtBDO processes

The above conclusion clearly indicates that the reconfiguration process has a significant advantage in reducing direct CO_2 emissions while improving the utilization rate of carbon elements. The next step is to consider the impact of electrification of utility engineering, that is, indirect carbon emissions. Indirect emissions mainly result from the use of electricity and steam. Indirect emissions are calculated based on the energy consumption of utilities. The thermal utility using coal produces 1 MJ of energy and emits 0.098 kg of CO_2 (Yousaf et al., 2022). Indirect CO_2 emissions from utilities that use electricity depend on the type of renewable energy sources, such as wind, solar, and wind-solar. The CO_2 emission factor of new energy power generation (wind-solar) is 23.3 kg/MW (Shi et al., 2020). The indirect carbon emissions of the conventional process and the reconfiguration process are shown in Figure.3b, which are 1,824 kg CO_2/t BDO and 379 kg CO_2/t BDO.

3.3 Energy analysis

Energy efficiency is the ratio of energy used effectively by a process to the actual energy consumed. In this study, the energy efficiency of the entire system is defined by Eq(2).

$$\gamma = \frac{E_{out}}{E_{in}} \quad (2)$$

where γ represents the energy efficiency, E_{out} is the product energy (MW), and E_{in} is the total energy consumption (MW), which is the energy of the raw materials, steam, and electricity.

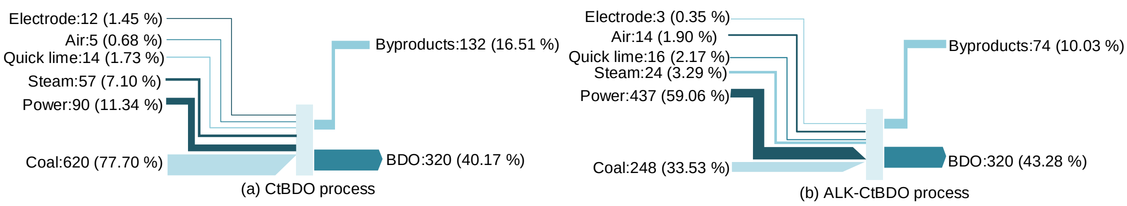

Figure 4: Energy structures of (a) CtBDO process, (b) ALK-CtBDO process, MW. Energy and its proportion contained in each stream input and output of each unit for two processes are shown in this figure. The width of the energy flow in the diagram stands for the energy amount in the stream. Unit of the values is MW

The energy structures of the CtBDO and ALK-CtBDO processes, based on the results of the simulated calculations, are shown in Figure 4. The width of the energy flow in the diagram is the energy amount in the stream. The energy efficiency of the conventional process and the reconstruction process is calculated to be 40.17 % and 43.28 %. The energy in BDO products is 320 MW in both CtBDO and ALK-CtBDO. However, the proportion of energy in the coal that accounts for the total energy input differs greatly because of high electricity input in the ALK-CtBDO; the proportions for the CtBDO and ALK-CtBDO are 77.70 % and 33.53 %, respectively. Electricity input in the ALK-CtBDO process is 437 MW, which accounts for 59.06 % of the total energy input. In ALK-CtBDO, the required energy is provided by renewable energy, which greatly reduces greenhouse gas emissions. Energy in by-products output differs significantly between the two processes. In CtBDO and ALK-CtBDO, the energy values are 132 MW and 74 MW, respectively. CtBDO accounts for 16.51 % of the total energy, while ALK-CtBDO accounts for 10.03 %. In addition, a significant amount of off-gas is generated in the CtM, CtH, and ETM units.

3.4 Economic analysis

Fixed capital investment (FCI) (Zhou et al., 2023) includes equipment purchases, construction, land and construction fees, pipeline and installation fees, project and supervision fees, unforeseen fees, instrumentation and control fees. Equipment investment can be calculated using Eq(3). Other investments related to the FCI are directly proportional to the equipment investment. This is expressed by Eq(4) as follows. The product cost is shown in Eq(5), which can be determined using the ratio estimation method (Yang et al., 2021). The exchange rate between the US dollar and the CNY is set at 7.23, and the total cost is expressed in CNY. The calculation process is based on 8,000 h/y of running time. Depreciation cost is calculated using 15 y of linear depreciation and a 4 % residual rate.

$$EI = \sum_j \theta \cdot EI_j^r \cdot (\frac{S_j}{S_j^r})^{sf} \quad (3)$$

$$FCI = EI \cdot (1 + \sum_{i=1}^{n} RF_i) \quad (4)$$

$$PC = C_r + C_u + C_{o\delta m} + C_d + C_{poc} + C_{ac} + C_{dsc} \quad (5)$$

where θ represents the domestic production index； EI^r_j is the reference of equipment j； S_j is the production scale of equipment j; S^r_j represents the reference scale of equipment j; Sf refers to the scale index; RF_i is the scale factor; C_r is the cost of raw materials; C_u is the cost of public utilities; $C_{o\&m}$ for maintenance and operating costs; C_d is the folding cost; C_{poc} is the manufacturing cost; C_{ac} is the management cost; C_{dsc} is the selling cost. The FCI of the conventional process is 25,667 CNY·t^{-1} BDO, while for the ALK-CtBDO process it is 20,994 CNY·t^{-1} BDO, representing a reduction of the conventional process, as illustrated in Figure 5a. The product costs for the conventional and reconfiguration processes, as shown in Figure 5b, are 9,869 and 14,467 CNY·t^{-1} BDO. The main factor contributing to the increase in product costs is the high cost of electricity from renewable energy sources.

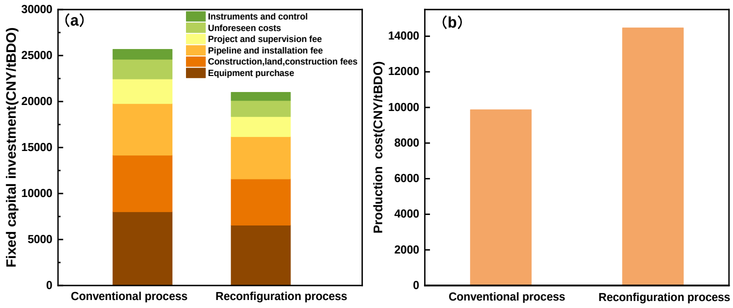

Figure 5: (a) Fixed capital investment of the two processes；(b) production costs of the two processes

The cost of renewable power can be significantly decreased with governmental fiscal support. At the same time, the production cost decreases. For instance, the price of solar photovoltaics is expected to decrease to approximately 0.2 CNY·kWh^{-1} and 0.13 CNY·kWh^{-1} in the years 2035 and 2050, respectively (LONGi, 2019), and the corresponding BDO cost will be reduced to 9,687 CNY·t^{-1} BDO and 8,120 CNY·t^{-1} BDO.

4 Conclusion

The study proposes a novel green process to enhance carbon utilization efficiency and reduce CO_2 emissions by integrating a coal-to-1,4-butanediol reconfiguration process with renewable energy hydrogen production. The reconfigured process improves the production of raw materials, such as formaldehyde and calcium carbide, provides green hydrogen to meet production needs by power-to-hydrogen unit, and uses renewable electricity for electrification to reduce indirect carbon emissions. The main conclusions from this study are as follows:

The reconfiguration process is regarded as environmentally friendly production due to carbon emissions of the process are reduced to 1,216 kg/t BDO. The carbon utilization efficiency is 99.10 % higher than that of the conventional CtBDO process. The energy efficiency of the reconfiguration process is slightly higher than that of the conventional process. The reconfiguration process demonstrates economic feasibility when the price of renewable power is less than 0.2 CNY·kWh^{-1}.

The reconfiguration process has demonstrated a remarkable potential in environmental performance. However, due to the high renewable power price, the economic performance is inevitably and substantially larger than that of conventional process. Fortunately, with the rapid development of renewable energy generation and power-to-hydrogen technologies, the price will continue to drop. We hope this work can provide a technological and economic basis for the future development of low-carbon energy to achieve the targeted climate benefits.

Acknowledgments

The authors would like to thank the Basic Research Innovation Group Project of Gansu Province (NO. 22JR5RA219)

References

Di Pretoro A., Silvetti A., Annesini M.C., 2023, Power-to-methanol process plant performances under uncertainty: economic and environmental criticalities. Chemical Engineering Transactions, 99, 110.

Chen C, Lu Y,Banares-Alcantara R, 2019, Direct and indirect electrification of chemical industry using methanol production as a case study. Applied Energy, 243, 71-90.

Luo P, Li X, 2021, Application and market of 1,4-butanediol production of Reppe method in China. Journal of Chemical Engineering, 9, 34.

Ma S, Lu S, Ma H, Li R, Xu C, Chen M, Zhang H, 2022, Energy and exergy analysis of a new calcium carbide production process. Fuel Processing Technology, 226, 107070.

Shi X, Qian Y, Yang S, 2020, Fluctuation analysis of a complementary wind–solar energy system and integration for large scale hydrogen production. ACS Sustainable Chemistry & Engineering, 8, 7097-7110.

Vollmer I, Jenks M J F, Roelands M, White R J, Harmelen T v, Wild P J d, Laan G P, Meirer F, Keurentjes J T F, Weckhuysen B M, 2020, Beyond mechanical recycling: giving new life to plastic waste. Angewandte Chemie (International Ed. in English), 59, 15402-15423.

Wang D, Meng W, Zhou H, Yang Y, Xie J, Yang S, Li G, 2022, Novel coal-to-methanol process with near-zero carbon emission: Pulverized coal gasification-integrated green hydrogen process. Journal of Cleaner Production, 339, 130500.

Xu M, Yan X, Li F, Xiao Y, Li J, Liu Z, He H, Li Y, Zhu Z, 2023, Fabrication high toughness poly(butylene adipate-co-terephthalate)/thermoplastic starch composites via melt compounding with ethylene-methyl acrylate-glycidyl methacrylate. International Journal of Biological Macromolecules, 250, 126446.

Yang Q, Zhang J, Chu G, Zhou H, Zhang D, 2021, Optimal design, thermodynamic and economic analysis of coal to ethylene glycol processes integrated with various methane reforming technologies for CO_2 reduction. Energy Conversion and Management, 244, 114538.

Yousaf M, Mahmood A, Elkamel A, Rizwan M, Zaman M, 2022, Techno-economic analysis of integrated hydrogen and methanol production process by CO_2 hydrogenation. International Journal of Greenhouse Gas Control, 115, 103615.

Zhao J, Gao J, Wang D, Chen Y, Zhang L, Ma W, Zhao S, 2024, Microwave-intensified catalytic upcycling of plastic waste into hydrogen and carbon nanotubes over self-dispersing bimetallic catalysts. Chemical Engineering Journal, 483, 149270.

Zhou H, Wang J, Meng W, Wang K, Li G, Yang Y, Fan Z, Wang D, Ji D, 2023, Comparative investigation of CO_2-to-methanol process using different CO_2 capture technologies. Fuel, 338, 127359.