Supporting Materials

Industrial ultra-low carbon methanol synthesis routes: techno-economic analysis, life cycle environment assessment and multi-dimensional sustainability evaluation

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This file contains: 14 pages, 3 sections, 1 figure, 11 tables.

Summary of figures and tables

1. Low carbon methanol synthesis route process data

Green low-carbon methanol project enterprises, processing capacity and output in China are listed in Table S1.

Table S1. Green low-carbon methanol project enterprises, processing capacity and output in China.

Items	Process	Scale	Raw material
Baofeng Energy	GH_2-CTM	6150000 t/a	Coal, Green H_2
Shanxi Coal Group Yulin chemical	GH_2-CTM	5600000 t/a	Coal, Green H_2
Yankuang XinJiang Energy&Chemical	GH_2-CTM	2200000 t/a	Coal, Green H_2
China Chemical Saiding Green energy Technology	BTM	380000 t/a	Biomass, Green H_2
Yuanhuo Energy	BTM	700000 t/a	Biomass, Green H_2
Goldwind green energy chemical industry	BTM	500000 t/a	Biomass, Green H_2
Cnina Energy Engineering Corporation Limited	BTM	300000 t/a	Biomass, Green H_2
Chifeng Green hydrogen chain Technology Co. LTD	BTM	300000 t/a	Biomass, CO_2, Green H_2

Approximate elemental analysis of crop straw and coal are shown in Table S2.

Table S2. Composition analysis of the feed coal and crop straw.

	Coal	Crop straw
Proximate analysis		
MOISTURE	9.54	5.53
FC	9.64	2.69
VM	39.45	80.79
ASH	50.91	11
Ultimate analysis		
C	74.455	45.01
H	4.955	6.09
N	1.585	0.6
Cl	2.44	0.043
S	0.065	0.15
O	6.84	40.04

Distribution of crude syngas components with different key gasification parameters are shown in Fig.S1.

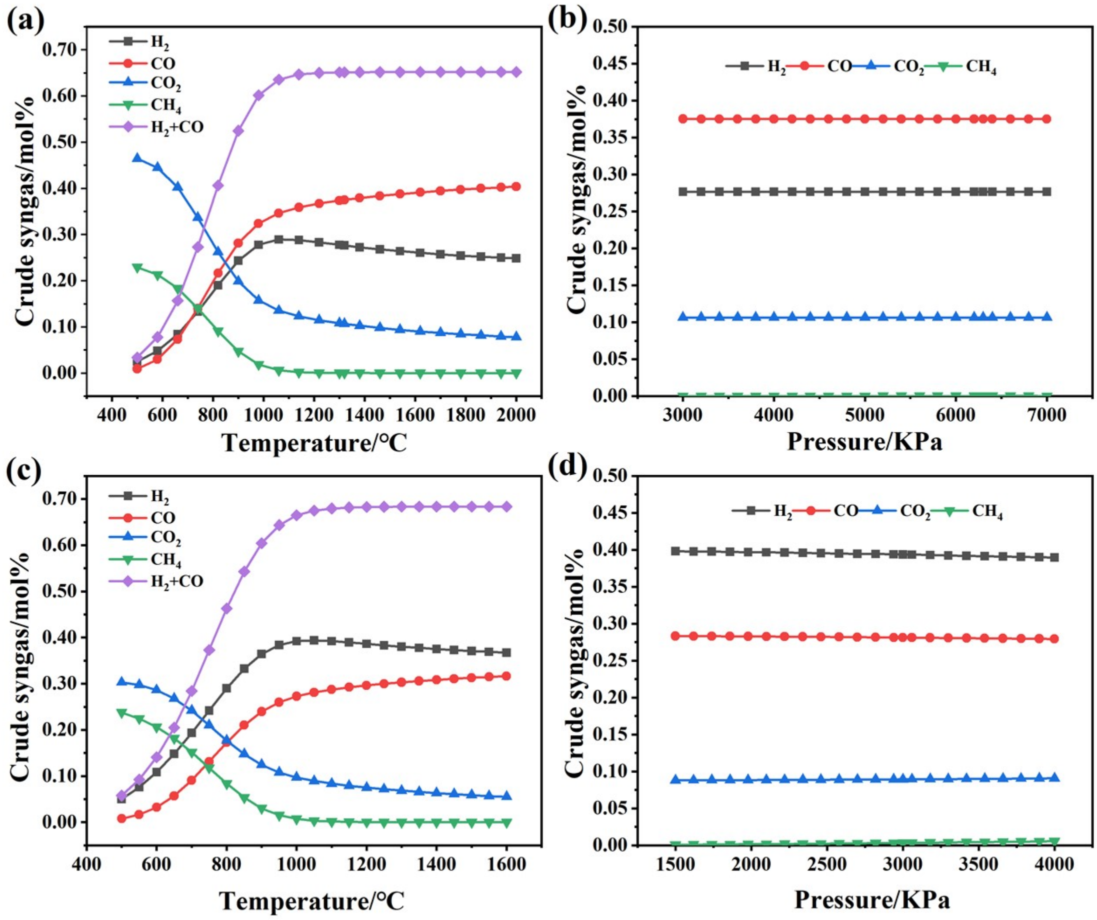

Fig.S1. Distribution of crude syngas components with different key gasification parameters: (a) Coal gasification temperature; (b) Coal gasification pressure; (c) Biomass gasification temperature; (d) Biomass gasification pressure

CTM, GH_2-CTM and BTM processes industry/ literature and simulation data are listed in the Table S3.

Table S3. CTM, GH2-CTM and BTM processes industry/ literature and simulation data.

`	Units	Industry/literature data[1]			Simulation data		
		CTM	GH_2-CTM	BTM	CTM	GH_2-CTM	BTM
Temperature	℃	1320		1050	1320		1050
Pressure	KPa	6300		3000	6300		3000
Coal/Biomass	t/h	1036.53		1188.46	1042.53		1188.46
O_2	t/h	839.81		-	860.06		200
（$CO+H_2$)	$\times 10^4$ Nm^3/h	168.69			168.37		168.46
Converted gas	t/h	156.78	130.51	-	162.02	132.32	87.55
Unconverted gas	t/h	693.79	847.9	-	677.16	832.92	747.34
Synthesis gas	t/h	850.57	978.41	850.57	839.18	965.24	834.89
GH_2 supplement	t/h	-	28.07	-	-	29.08	-
Methanol	t/h	780.94	926.88	780.94	774.48	924.02	786.79
Purge gas	t/h	23.62	25.3	23.62	26.42	27.77	17.14

2. Technical and economic analysis

Cost estimation of purchase equipment cost and total capital investment are listed in the Table S4.

Table S4. Cost estimation of purchase equipment cost and total capital investment.

Parameter	Benchmark	S_0	TCI_0, M$	α	S_{CTM}	TCI_{CTM}, M$	$S_{CTM\text{-}GH2}$	$TCI_{CTM\text{-}GH2}$, M$	S_{BTM}	TCI_{BTM}, M$	Ref. year	Ref.
		Reference			**CTM**		**CTM-GH_2**		**BTM**			
ASU	O_2 supply (kg/s)	21.3	45.7	0.5	238.9	177.63	159.27	145.04	79.6	102.54	2018	[2]
RAPT	Raw coal (kg/s)	27.4	29.1	0.67	289.6	163.94	289.6	163.94	\	\	2018	[2]
	Straw (t/h)	33.5	11.46	0.85	\	\	\	\	1188.5	421.02	2002	[3]
GU	Coal input (t/d)	9000	148.05	0.67	25020	340.89	25020	340.89	\	\	2018	[4]
	Biomass input (t/d)	2000	63.4	0.67	\	\	\	\	28523	500.96	2007	[5]
WGS	$CO+H_2$ (kmol/h)	8819	14.4	0.65	38312	49.82	30048	42.54	22543	35.30	2007	[5]
AGR	CO_2 removal (t/h)	327	64.6	0.67	1368	195.59	1161	175.23	809	137.56	2018	[2]
MS	Feed syngas (kmol/s)	10.8	20.4	0.29	20.8	28.63	24.8	30.13	20.8	28.63	2018	[2]
MD	Feed methanol (kg/s)	3.66	1.72	0.65	215.1	28.20	256.7	31.63	218.6	28.49	2018	[2]
Electrolyzer	Feed H_2 (t/d)	50	53.2	0.92	\	\	697.92	692.67	\	\	2019	[6]

CEPCI of different years is shown in Table S5.

Table S5. CEPCI of different years.

	Years	Value	Ref.
CEPCI	2021	699.7	[7]
	2019	607.5	[7]
	2018	603.1	[7]
	2017	567.5	[8]
	2007	525.4	[8]
	2002	395.6	[8]

The prices of raw materials, products, utilities and transportation involved in the three synthetic routes are shown in Table S6. Among them, the price of green hydrogen is simply estimated, and the formula is shown as S1. Electricity price has the greatest influence on the cost of green hydrogen, and the price distribution of green hydrogen under different electricity prices is shown in Table S7.

$$TPC_{GH_2} = P_e \times EC_e + P_w \times EC_w + P_i + P_m + P_s \quad \text{(S1)}$$

TPC_{GH_2} represents the price of green hydrogen, the unit is CNY/t; P_e represents the price of electricity, the unit is CNY/kwh; EC_e represents the electricity consumption, the unit is kwh; P_w represents the price of water, the unit is CNY/t; EC_w represents the water consumption, the unit is t; P_i, P_m, P_s respectively represents the depreciation cost of electrolytic cell equipment, maintenance costs and staff salaries , the unit is CNY/t .

Table S6. The prices of raw materials, products, utilities and transportation involved in the three synthetic routes.

Items		Units	Price	Ref.
Coal		CNY/t	400	
Straw		CNY/t	450	
LP steam		CNY/t	170.22	9
MP steam		CNY/t	200.26	9
HP steam		CNY/t	220.24	9
Cooling water		CNY/t	0.34	9
Electricity		CNY/kwh	0.4	10
Fuel coal		CNY/t	800	10
Refrigerant(-40℃)		CNY/GJ	46.2	9
Transportation	Coal/Biomass-Railway	CNY/t·km	0.167	
	Coal/Biomass-Highway	CNY/t·km	0.37	

	H_2-Highway	CNY/tH_2·km	78.12	[11]
	O_2-Highway	CNY/tO_2·km	3.92	[12]

Table S7. The price distribution of green hydrogen under different electricity prices.

Items	Value					
Electricity price	0.4	0.35	0.3	0.25	0.2	0.13
Green H_2 price	19526.6	17276.6	15026.6	12776.6	10526.6	7376.6

The outcomes of fixed investment and cost estimation are shown in Table S8.

Table S8. Detailed results of techno-economic analysis.

Items	CTM	GH2-CTM	BTM
Production scale (t/h)	770	918	772
Fixed investment (M$)	984.7	929.4	1254.5
Raw Material cost (CNY/t)	541.6	1071.8	692.1
Pretreatment cost (CNY/t)	34.4	28.9	101.9
Transportation cost (CNY/t)	163.2	152.4	202.4
Utilities cost (CNY/t)	1081.6	891.6	999.6
Employee salary (CNY/t)	3.2	2.7	4.9
Maintenance and depreciation cost (CNY/t)	78.3	62.1	99.5
Administrative and overhead cost (CNY/t)	40.7	46.3	45.4
Marketing cost (CNY/t)	38.1	44.2	42.1
Total production cost (CNY/t)	**1981.1**	**2299.9**	**2187.9**

3. Life cycle environmental assessment

The unified converted value of the energy-consuming working medium is listed in the Table S9.

Table S9. The unified converted value of energy consuming working medium.[13]

Items	Energy conversion value[a] (kgEo)
LP steam (1.0 MPa, 125℃)	76/t
MP steam (4.0 MPa, 180℃)	88/t
HP steam (10.0 MPa, 250℃)	92/t
Electricity	0.22/kwh
Cooling water	0.06/t
Fuel coal	700/t
Refrigerant(-50℃)	0.06/MJ

a: This standard stipulates that the data unit of energy consumption is kgEo, and the energy consumption data unit of the calculation results under this standard is converted to kgce. (1 kgEo≈1.4286 kgce)

GHG indirect emission factors are listed in the Table S8.

$$IE_{CO_2} = I_{CO_2} \times LHV_{CO_2} \times EC \times 44/12 \quad \text{(S2)}$$

$$IE_{CH_4} = I_{CH_4} \times LHV_{CH_4} \times EC \quad \text{(S3)}$$

$$IE_{N_2O} = I_{N_2O} \times LHV_{N_2O} \times EC \quad \text{(S4)}$$

Where IE represents an indirect emission, unit is tCO_2; I is indirect emission factor, unit is $t{\cdot}CO_2/MJ$; EC is process energy consumption quality, unit is t; LHV is the low calorific value, unit is MJ/t. Emission data is calculated according to Formula S2-S4.

Table S10. The indirect GHG emission factors.[14]

Items	LHV (MJ/t)	I_{CO_2}(tCO_2/MJ)	I_{N_2O} (tCO_2/MJ)	I_{CH_4} (tCO_2/MJ)
Standard oil	41868	25.33×10^{-6}	0.41×10^{-9}	0.07×10^{-6}
Standard coal	29308	5.73×10^{-6}	0.17×10^{-9}	0.43×10^{-6}
Crude oil	41816	16×10^{-6}	0.27×10^{-9}	0.05×10^{-6}
Crude coal	20908	4.26×10^{-6}	0.06×10^{-9}	0.42×10^{-6}
Fuel gas	45998	25.33×10^{-6}	0.41×10^{-9}	0.07×10^{-6}
Fuel oil	41816	25.33×10^{-6}	0.41×10^{-9}	0.07×10^{-6}
Fuel coal	29308	5.73×10^{-6}	0.17×10^{-9}	0.43×10^{-6}
Electricity[a]	10.89	248.02×10^{-6}	0.62×10^{-9}	2.16×10^{-6}

a: Unit is kW·h

PFCF in Table S11 represents the energy consumption factor, unit is MJ/MJ; and LHV is the low calorific value, unit is MJ/t.

Table S11. The primary consumption factor of NED.[14]

Items	LHV (MJ/t)	$PFCF_{Crude\ oil}$ (MJ/MJ)	$PFCF_{Crude\ coal}$ (MJ/MJ)	$PFCF_{Crude\ gas}$ (MJ/MJ)
Standard oil	41868	1.06	0.14	0.03
Standard coal	29308	0.11	1.06	0.00
Crude oil	41816	1.05	0.1	0.02
Crude coal	20908	0.00	1.05	0.00
Fuel gas	45998	1.06	0.14	0.03
Fuel oil	41816	1.06	0.14	0.03
Fuel coal	29308	0.11	1.06	0.00
Electricity[a]	10.89	0.37	2.86	0.03

a: Unit is Kw/h.

References

1. Z. Bai, Q. B. Liu, L. Gong and J. Lei, *Appl. Energy*, 2019, **243**, 91-101.
2. H. Huang, S. Y. Yang and P. Z. Cui, *Energy Conv. Manag.*, 2018, **157**, 186-194.
3. C. N. Hamelinck, A. P. C. Faaij, H. den Uil and H. Boerrigter, *Energy*, 2004, **29**, 1743-1771.
4. Y. J. Zhao, Q. Liu, Y. Y. Duan, Y. K. Zhang, Y. Huang, L. J. Shi, J. C. Wang and Q. Yi, *Energy Conv. Manag.*, 2022, **268**, 20.
5. H. F. Zhang, L. G. Wang, M. Pérez-Fortes, J. Van Herle, F. Maréchal and U. Desideri, *Appl. Energy*, 2020, **258**, 14.
6. D. D. James B, Huya-Kouadio J, *Analysis of advanced H2 production & delivery Pathways.*, https://www.hydrogen.energy.gov/docs/hydrogenprogramlibraries/pdfs/review18/pd102_james_2018_p.pdf, 2018.
7. R. Junsittiwate, T. R. Srinophakun and S. Sukpancharoen, *Energy Sustain Dev.*, 2022, **66**, 140-150.
8. E. Adu, Y. D. Zhang, D. H. Liu and P. Tontiwachwuthikul, *Energies*, 2020, **13**, 28.
9. J. X. Liu, X. Zhou, G. F. Yang, H. Zhao, Z. B. Zhang, X. Feng, H. Yan, Y. B. Liu, X. B. Chen and C. H. Yang, *Chin. J. Chem. Eng.*, 2023, **57**, 290-308.
10. *Sinopec Project Feasibility Study Technical Economy-Parameter & Data.*, Sinopec Economic & Development Research Institute., 2021.
11. Y. J. Zhao, Q. Liu, Y. Y. Duan, Y. K. Zhang, Y. Cui, Y. Huang, D. Gao, L. J. Shi, J. C. Wang and Q. Yi, *Int. J. Hydrog. Energy*, 2022, **47**, 19338-19352.
12. M. Balys, E. Brodawka, A. Korzeniewska, J. Szczurowski and K. Zarebska, *Sci. Total Environ.*, 2021, **786**, 14.
13. *Standard for calculation of energy consumption in petrochemical engineering design. GB/T 50441-2016.*, 2016.
14. X. Zhou, H. Yan, X. Feng, H. Zhao, Y. B. Liu, X. B. Chen and C. H. Yang, *Ind. Eng. Chem. Res.*, 2020, **59**, 20086-20101.