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Aspen Simulation of a Coal-to-Ethylene Glycol Production Process

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Ethylene glycol (EG) is an important chemical raw material with wide-ranging applications, including its use as a solvent, refrigerant, antifreeze, raw material for polyester resins, as well as in the production of pharmaceuticals, coatings, and cosmetics. Coal-to-EG is an important part of extending the coal chemical industry chain, mainly involving reactions such as carbon monoxide coupling to produce dimethyl oxalate and hydrogenation of dimethyl oxalate to produce EG. In this work, the full process simulation of a coal-to- EG plant with an annual production of 220,000 t/y EG was conducted using Aspen Plus software. It mainly includes units such as the carbon monoxide coupling unit, the intermediate product methyl nitrite regeneration unit, the dimethyl oxalate hydrogenation unit, the product refining unit, and the by-product recovery unit. The simulation results of all the units were obtained based on the accurate simulation procedure, which can provide reference and guidance for the subsequent actual production process of coal-to-EG, and also provide strong support for the optimization of the coal-to-EG process in the future.

1. Introduction

Ethylene glycol (EG) is a versatile chemical compound with a wide range of industrial applications, commonly used as a solvent, antifreeze, and raw material in various industries. Methods for producing EG can be divided into petroleum-based routes and non-petroleum-based routes (Sulaiman et al. 2021). The petroleum-based route utilizes ethylene as the raw material, which is obtained through the production of ethylene oxide. Non-petroleum-based routes utilize synthesis gas as the raw material and can employ various methods to synthesize EG. Currently, major large-scale EG production facilities worldwide primarily adopt the petroleum-based route, also known as the ethylene route. In this route, ethylene oxide is produced by directly oxidizing ethylene with oxygen in the presence of silver catalysts, methane or hydrogen as stabilizers, and chloride inhibitors. Ethylene oxide then undergoes a subsequent reaction directly with water or under catalytic conditions to produce EG. Although the petroleum-based route has matured over the years, it has high water consumption, generates multiple by-products during production, and is significantly affected by fluctuations in petroleum prices, thereby remaining dependent on petroleum resources (Chu et al. 2022). Especially in recent years, amidst continuous conflicts in the Middle East region, the advantages of the petroleum-based route have become less apparent. Conversely, synthesis gas is widely available, can be separated and purified from coal, and can also be extracted from industrial waste gases, making it more advantageous for development compared to petroleum (Yang et al. 2022).

Process simulation optimizes coal-to-EG production by modelling reaction and thermodynamics, enabling condition optimization, minimizing by-products, integrating energy-saving measures, and improving product quality and economics. However, the whole process simulation of the coal-to-EG plant including the carbon monoxide coupling unit, methyl nitrite regeneration unit, dimethyl oxalate hydrogenation unit, product refining unit, and by-product recovery unit are not reported yet.

The primary objective of this work is to simulate a coal-to-EG plant with capacity of 220,000 t/y EG using Aspen Plus. This simulation holds paramount importance in advancing the efficiency and sustainability of coal-based EG production, offering insights crucial for process optimization and facilitating improvements in chemical manufacturing.

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2. Aspen simulation

Considering the correlation between the raw materials, products, and operational conditions of the coal-to-EG process, NRTL-RK method is used as the global physical property model. The main reactions are listed in Table 1 (Yue et al. 2012).

Table 1: The main reaction conversions

No.	Reaction equation	Conversion	Unit	Abbreviation
1	4 NO + O_2 + 4 CH_3OH → 4 CH_3NO_2 + 2 H_2O	O_2: 1	Methyl nitrite regeneration	CH_3NO_2: methyl nitrite, MN
2	2 CO + 2 CH_3NO_2 → $C_4H_6O_4$ + 2 NO	MN: 0.91488	Carbon monoxide coupling	$C_4H_6O_4$: dimethyl oxalate, DMO
3	CO + 2 CH_3NO_2 → $C_3H_6O_3$ + 2 NO	MN: 0.04512		$C_3H_6O_3$: dimethyl carbonate, DMC
4	$C_4H_6O_4$ + 2 H_2 → $C_3H_6O_3$ + CH_3OH	DMO: 1	Dimethyl oxalate hydrogenation	
5	$C_3H_6O_3$ + 2 H_2 → $C_2H_6O_2$ + CH_3OH	DMC: 0.95		$C_2H_6O_2$: ethylene glycol, EG
6	$C_2H_6O_2$ + H_2 → C_2H_5OH + H_2O	DMC: 0.01		
7	2 $C_2H_6O_2$ + H_2 → $C_4H_{10}O_2$ + 2 H_2O	DMC: 0.01		$C_4H_{10}O_2$: 1,3-butylene glycol
8	3 $C_2H_6O_2$ + H_2 → 2 $C_3H_8O_2$ + 2 H_2O	DMC: 0.01		$C_3H_8O_2$: 1,2-propylene glycol, PG

Taking a coal-to-EG production rate of 220,000 t/y as an example, the process was divided into five units, including the carbon monoxide coupling unit, methyl nitrite regeneration unit, dimethyl oxalate hydrogenation unit, product refining unit, and by-product recovery unit. Subsequently, a full-process simulation was conducted, with Aspen screenshots provided in Figure 1.

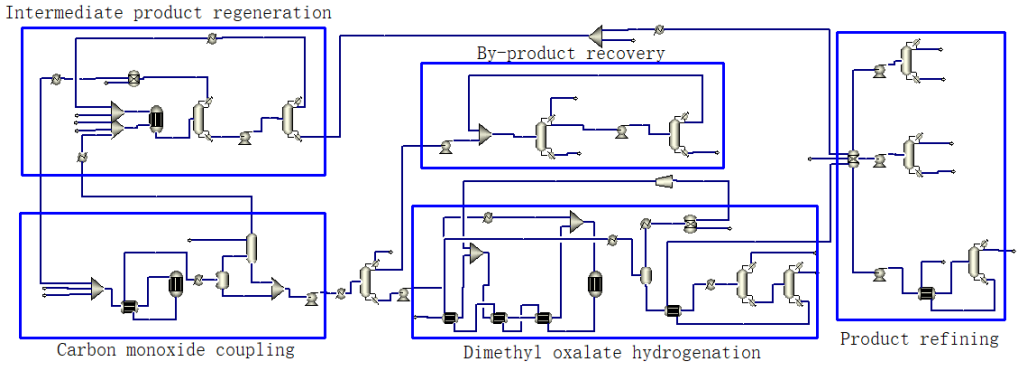

Figure 1: Whole process model in Aspen Plus

3. Simulation results

3.1 Raw materials and products

Table2 lists the whole mass balance of the coal-to-EG process. Utility consumptions are presented in Table 3.

Table 2: Mass balances of the coal to EG process

Raw material	Consumption(t/y)	Product	Yield(t/y)
CO	225,733	EG	223,538
H_2	31,156	DMC	16,897
CH_3OH	192,122	PG	1,644
NO	61,625	1,3-butylene glycol	1,548
O_2	66,184		
N_2	224		

Table 3: Utility consumptions of the coal to EG process

Utility	Unit	Value	Utility	Unit	Value
Cooling water	t/h	151,129.7	HP steam	t/h	8.94
Electricity	kW	3,596.23	MP steam	t/h	143.75
Fuel gas	MW	9.58	LP steam	t/h	818.09

The consumption of CO is 225,733 t/y, H_2 is 31,156 t/y, methanol is 192,122 t/y, NO is 61,625 t/y, O_2 is 66,184 t/y, and N_2 is 224 t/y. Ultimately, the production yield includes 223,538 t/y of EG, along with by-products such as 16,897 t/y of DMC, 1,644 t/y of PG, and 1,548 t/y of 1,3-butylene glycol.

3.2 Mass balances of carbon monoxide coupling unit

The screenshot and mass balances of the carbon monoxide coupling unit are shown in Figure 2 and Table 4.

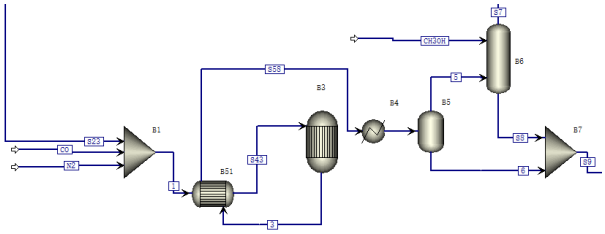

Figure 2: Flowsheet of the carbon monoxide coupling unit

In the carbon monoxide coupling unit, the total inlet stream flow rate for S23 is 308,651 kg/h, comprising significant amounts of CO, N_2, and MN. Following the reaction, the outlet streams S7 and S9 show considerable changes in composition. Outlet stream S7 contains CO, N_2, MN, NO, and CH_3OH, indicating the conversion of reactants. Outlet stream S9 primarily consists of DMO, CH_3OH and DMC, with traces of CO, N_2, MN, and NO. These transformations highlight the efficiency of the coupling process, where raw materials are converted into valuable intermediate products, essential for the subsequent stages of EG production.

Table 4: Mass balances of carbon monoxide coupling unit

Items	Inlets				Outlet	
Stream name	CO	N2	CH3OH	S23	S7	S9
Temperature/°C	30	30	30	30	4.3	37.5
Pressure/bar	1.01	1.01	8	1.01	1.01	1.01
			Mass flowrate (kg/h)			
CO	28	0	0	31,428	31,430	6
N_2	0	28	0	211,639	211,640	28
MN	0	0	0	65,584	2,584	40
DMO	0	0	0	0	0	58,041
DMC	0	0	0	0	0	2,183
NO	0	0	0	0	30,947	3.61
CH_3OH	0	0	21,949	0	16,960	4,989

3.3 Mass balances of methyl nitrite regeneration unit

The screenshot and mass balances of the intermediate product methyl nitrite regeneration unit are shown in Figure 3 and Table 5.

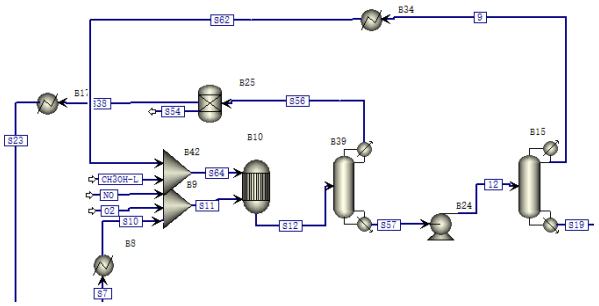

Figure 3: Flowsheet of the methyl nitrite regeneration unit

In the intermediate product regeneration unit, the process involves crucial steps to recover and regenerate intermediate products, primarily focusing on CH_3OH, O_2 and NO. This stage ensures the efficient use of raw

materials and minimizes waste, contributing to the overall sustainability of the coal-to-ethylene glycol process. The inlet streams, which include significant quantities of CH_3OH, NO, and O_2, undergo esterification reactions. After-reaction, water is primarily removed, while unreacted CH_3OH and NO are recycled back into the unit. This regeneration not only reduces the demand for fresh raw materials but also lowers operational costs and environmental impact. The process efficiency in this unit is critical, as it directly influences the yield and purity of the final EG product, making it a vital component of the overall production workflow.

Table 5: Mass balances of methyl nitrite regeneration unit

Items	Inlets				Outlet		
Stream name	CH3OH-L	NO	O2	S10	S19	S54	S23
Temperature/°C	45	35	35	35	105.07	-3.56	30
Pressure/bar	1.01	1.01	1.01	1.01	1.21	1.01	1.01
			Mass flowrate (kg/h)				
CO	0	0	0	31,430	0	0	31428
N_2	0	0	0	211,640	0	0	211639
MN	0	0	0	2,583.67	0	125	65584
NO	0	7,703	0	30,947	0	7,619	0
O_2	0	0	8,273	0	0	0	0
H_2O	48	0	0	0	9363	0.21	0
CH_3OH	25,863	0	0	16,960	0	9,685	0

3.4 Mass balances of dimethyl oxalate hydrogenation unit

The screenshot and mass balances of the DMO hydrogenation unit are shown in Figure 4 and Table 6.

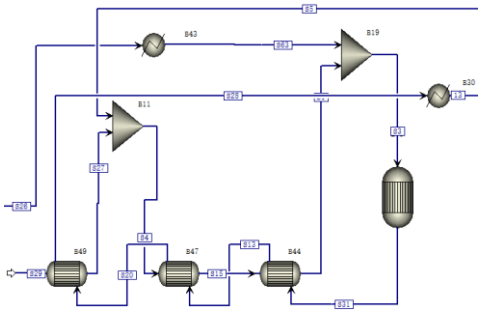

Figure 4: Flowsheet of the dimethyl oxalate hydrogenation unit

Table 6: Mass balances of dimethyl oxalate hydrogenation unit

Items	Inlets			Outlet
Stream name	S26	S29	S5	13
Temperature/°C	170.96	25	91.93	30
Pressure/bar	25	25	25	24.9
		Mass flowrate (kg/h)		
DMO	58,041	0	0	0
DMC	9	0	0	9
H_2	0	3,894	72,558	72,573
H_2O	0	0	0.16	223
CH_3OH	0.0044	0	63	30,772
C_2H_5OH	0	0	0	215
MG	0	0	0	2,214
PG	0	0	0	232
1,3-Butylene glycol	0	0	0	208
EG	0	0	0	28,120

In the DMO hydrogenation unit, the process involves three main inlet streams with all pressures set at 25 bar. The inlet stream S26, at a temperature of 170.96°C, has a total flow rate of 58,050 kg/h (comprising DMO, DMC, and CH_3OH). Inlet stream S29, at 25°C, has a flow rate of 3,894 kg/h (all H_2), and inlet stream S5, at 91.93°C, has a flow rate of 72,621 kg/h (including H_2, H_2O, and CH_3OH). After the hydrogenation reaction, the outlet

stream 13, at 30°C and 24.9 bar, has a total flow rate of 134,567 kg/h. This stream includes DMC, H_2, H_2O, CH_3OH, C_2H_5OH, MG, PG, 1,3-butylene glycol, and EG. This stage effectively demonstrates the hydrogenation process's efficiency in converting DMO to EG while managing significant flow rates and compositions.

3.5 Mass balances of product refining unit

The screenshot and mass balances of the product refining unit are shown in Figure 5 and Table 7. The parameters of the three columns are listed in Table 8.

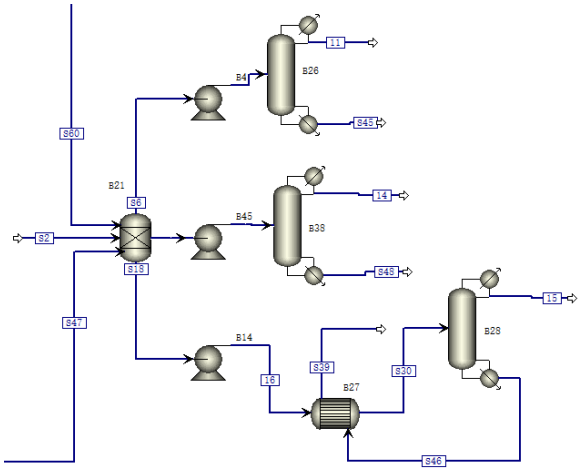

Figure 5: Flowsheet of the product refining unit

The product refining unit effectively processes inlet streams to separate and refine components. Inlet streams include S2 (1,436 kg/h CH_3OH), S60 (1,436 kg/h H_2O), and S47 (28,608 kg/h, including MG, PG, 1,3-butylene glycol, and EG). After-refinement, 27940 kg/h EG in S39 is produced with 99.99% purity; 231 kg/h PG in S48 is produced. This refining step demonstrates efficient separation and purification, aligning well with the tabulated data and emphasizing the effectiveness of the refining process without redundancy.

Table 7: Mass balances of product refining unit

Items	Inlets			Outlet					
Stream name	S2	S47	S60	11	S45	14	S48	15	S39
Temperature/°C	40	40	45	81.79	197.34	72.43	187.22	78.57	68.57
Pressure/bar	1.01	2.2	1.2	1.01	1.21	1.01	1.21	1.01	1.21
				Mass flowrate (kg/h)					
H_2O	0	0	1,436	603	0.55	329	0.9	502.58	0
CH_3OH	1,436	0	0	287	0	689	0	459	0
MG	0	56	0	0	0	0	0	54	2
PG	0	232	0	0	0		231	0.032	1
1,3-Butylene glycol	0	208	0	0	207	0	0	0.0094	1
EG	0	28,112	0	0	0	0	0	172.3	27,940

Table 8: Parameters of all the columns

Units	Product refining unit			By-product recovery unit	
Block name	B26	B38	B28	B16	B18
Top temperature/°C	82	72	79	64	137
Top pressure/bar	1.2	1.2	1.2	1.2	10
Number of stages	20	20	20	30	14
Feed stage	8	8	8	5	12
Reflux ratio	3	3	5	5.3	7.5

3.6 Mass balances of by-product recovery unit

The screenshot and mass balances of the by-product recovery unit are shown in Figure 6 and Table 9.

The by-product recovery unit efficiently separates MN, DMC, and methanol from the inlet stream. The process handles varying temperatures and pressures, starting with an inlet stream S32 at 65.81°C and 10 bar, with a flow rate of 6,298.13 kg/h. Through recovery, three key outlet streams are obtained: S25 at 138.03°C and 10.3 bar, S22 at 95.79°C and 1.21 bar, and S24 at 64.09°C and 1.01 bar, each showing significant reduction or separation of MN, DMC, and CH_3OH. This efficient recovery aligns well with the data presented in the tables, emphasizing the process's effectiveness without redundancy.

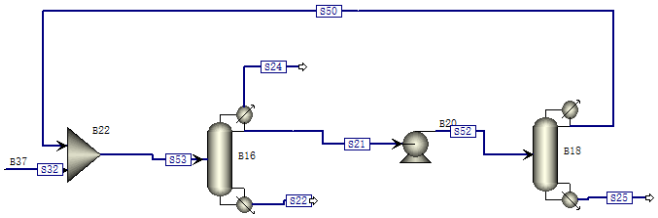

Figure 6: Flowsheet of the by-product recovery unit

Table 9: Mass balances of by-product recovery unit

Items	Inlets		Outlet	
Stream name	S32	S22	S24	S25
Temperature/°C	66	96	64	138
Pressure/bar	10	1.21	1.01	10.3
	Mass flowrate (kg/h)			
MN	14	0	14	0
DMC	2,029	2,004	0.31	24
CH_3OH	4,256	1	469	3,785

4. Conclusion

The coal-to- EG process holds significant promise as a sustainable alternative to traditional petroleum-based routes, offering diversification and resilience to the chemical industry. Through comprehensive process simulation using Aspen Plus software, this study simulated a production scale of 220,000 t/y, delineates the complex series of reactions and unit operations involved in coal-based EG production.

The simulation results reveal the consumption rates of various feedstocks, including CO, H_2, methanol, NO, O_2, and N_2, as well as the production yields of EG and associated by-products such as DMC, PG, and 1,3-Butylene glycol.

The findings of this study have significant implications for the design, operation, and optimization of coal-based EG production plants. By providing a comprehensive understanding of process dynamics and performance characteristics, process simulation serves as a powerful tool for process engineers and researchers alike.

Acknowledgments

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