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Process Synthesis and Optimization: A P-graph Approach for Cost, Emission, and Waste Minimization

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Waste and emissions cause major challenges in chemical plants due to their environmental impact, high cost of treatment, regulatory penalties, disposal fees, and potential loss of process efficiency. Current process synthesis methods do not consider those aspects from the process synthesis and design level. This work presents a methodology that provides a more comprehensive reaction route analysis for the process synthesis, focusing on the screening of alternative production pathways, derived from known reaction sequences, for acrylic acid synthesis, integrating economic and environmental metrics using the P-graph tool. The study demonstrates the benefits of sustainable process synthesis, highlighting how P-graph enables the rigorous evaluation and selection of the most energy-efficient and low-emission pathways as well as the sub-optimal pathways. The proposed methodology is applied to the synthesis and optimization of an acrylic acid production process, integrating economic and environmental metrics within a P-graph superstructure to evaluate multiple production pathways. The results emphasize the importance of incorporating economic and environmental factors into process design for more accurate analysis, and how P-graph can support sustainable decision-making in industrial settings.

1. Introduction

The chemical industry plays a pivotal role in modern society through supplying essential products, including fuels, fertilizers, polymers, and pharmaceuticals (Pinheiro Pires et al., 2021). However, its processes are often accompanied by significant environmental challenges such as high energy consumption, greenhouse gas emissions, and substantial waste generation (Abubakar et al., 2024). As a result, integrating sustainability into chemical process design has become increasingly crucial (Pimentel et al., 2022).

In early-stage design, production pathway screening is commonly performed using economic-based criteria that prioritize the most profitable reaction routes. For example, the Economic Potential (EP) method (Seider et al., 2016) estimates profitability as the difference between the total value of products and the cost of raw materials. Metrics such as Net Present Value (NPV) and Internal Rate of Return (IRR) are also often applied. However, these methods typically overlook environmental impacts like emissions, utility demands, or waste. Moreover, traditional optimization models are often either too simplistic or computationally intensive when applied to large-scale chemical reaction networks (Blömer et al., 2024).

One major challenge in conventional pathway analysis approaches, such as the hierarchical design methodology (Douglas, 1988) or five-step synthesis framework (Seider et al., 2016), is the lack of integration of sustainability indicators in early decision-making. The P-graph framework, introduced by Friedler et al. (1992), offers a graph-theoretic approach to systematically generate and evaluate feasible process configurations using Maximal Structure Generation (MSG) and Solution Structure Generation (SSG). It has been widely applied in sustainability-focused system design, including bio-based systems (Pinheiro Pires et al., 2021), carbon footprint reduction, and wastewater networks (Pimentel et al., 2022). However, despite these advancements, the use of P-graph for screening chemical production pathways, where each pathway represents a sequence of reactions and process-level performance, is still limited in the literature (Benjamin et al., 2021). Most studies focus on broader system synthesis rather than evaluating and comparing competing chemical routes based on combined

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economic and environmental indicators. There remains a need for a decision-support framework that enables integrated screening of chemical production alternatives. This study bridges the gap between high-level reaction route identification and process-level decision-making by evaluating each production pathway as a single operating block enriched with economic and sustainability indicators. This paper introduces a P-graph approach that simplifies the identification of optimal production pathways by incorporating environmental and economic indicators without the need for complex mathematical formulations.

2. Methodology

The P-graph software is freely accessible online for download and use. It employs a bipartite graph structure consisting of two types of nodes: M-type (representing materials) and O-type (representing operations). In traditional process network synthesis (PNS), material flows—both inputs and outputs—are depicted as M-type nodes, which are linked to O-type nodes denoting process operations (Friedler et al., 1992). The software then utilizes the Accelerated Branch-and-Bound (ABB) algorithm to generate both optimal and near-optimal network configurations. This study proposes a structured and replicable methodology for screening and optimizing production pathways based on economic and environmental criteria on a synthesis level.

2.1 Step 1: Target chemical product selection

The process starts by identifying the target chemical and its properties, such as the price, market demand, and required capacity. Data is a crucial aspect of this methodology, and the more accurate the data, the more accurate the selection for the decision-making process. Data can be obtained through the review of literature and relevant industrial reports. In this research, the chosen product as a case study is acrylic acid with an assumed capacity of 96,000 t/y.

2.2 Step 2: Identification of potential production pathways

All feasible production pathways for acrylic acid were identified through literature review, with each route representing a complete sequence of reactions modeled as a single production block. Detailed mechanistic modeling of intermediate reaction steps was beyond the intended system-level scope of this work. For this case study, three main routes were included and studied as shown in Table 1 (Puwar and Jalan, 2016)

Table 1: Product pathways summary

Pathway Name	Reaction	Catalysts	Operating conditions
Sequential dehydration and oxidation of glycerol	Glycerol → Acrolein → Acrylic Acid	Acidic solid catalysts and mixed metal oxides	250–300 °C, 1 atm or slightly above
Acrylic acid from ethylene	Ethylene + CO + H_2O → Acrylic Acid	Ag-based and Rh or Co catalysts	300–400 °C, or slightly above
Acrylic acid from propylene	Propylene + O_2 → Acrolein → Acrylic Acid	Mixed metal oxides	250–300 °C, 1 atm or slightly above

2.3 Step 3: Production pathways economic and environmental factors consideration

Economic data is collected for all chemical species involved, including market prices for raw materials and products. The main product and byproduct sales are the revenue streams. In addition, capital expenditures (CAPEX) and operating expenditures (OPEX) for each production pathway are either obtained from literature or estimated based on existing analogous processes from industry. This helps in getting a more accurate and realistic consideration of economic factors in the model.

The environmental performance indicators are also identified for each production pathway. These include carbon dioxide emissions, wastewater production, and utility demands such as electricity, steam, and cooling water. The total CO_2 emissions, E_{total}, is estimated as shown in Eq(1) as the summation of CO_2 produced from the main and side reactions, $E_{reactions}$, emissions associated with heating processes and steam generation, $E_{heating}$, and power used from the grid, E_{power}. This helps in providing a deeper environmental analysis and constrains the system. Eq(2) shows the correlation between power consumed, $P_{consumed}$, and steam consumed, $S_{consumed}$, to the CO_2 emissions by using correlation factors where $f_{NG\ emission}$ is the natural gas production emission factor, E_{steam} is the enthalpy of steam, and $f_{electricity\ emission}$ is the electricity emission factor (Marjanović and Mrzljak, 2021). All the factors and their values are shown in Table 2.

$$E_{total} = \sum(E_{reactions} + E_{heating} + E_{power}) \quad (1)$$

$$E_{heating} + E_{power} = (S_{consumed} \times E_{steam} \times f_{NG\ emission}) + (P_{consumed} \times f_{electricity\ emission}) \quad (2)$$

The same goes with the wastewater generation. As shown in Eq(3), where the total wastewater generation, WW_{total}, is considered from the main and side reactions, $WW_{reactions}$, steam condensation, $WW_{heating}$, and cooling water blowdown, $WW_{cooling}$. Eq(4) is the equation relating the steam consumed, $S_{consumed}$, and cooling water consumed, $CW_{consumed}$, with the wastewater generation by using condensate loss factor, $f_{condensate\ loss}$, and blowdown rate, $R_{blowdown}$ (Elwardany, 2024).

$$WW_{total} = \sum(WW_{reactions} + WW_{heating} + WW_{cooling}) \quad (3)$$

$$WW_{heating} + WW_{cooling} = (S_{consumed} \times f_{condensate\ loss}) + (CW_{consumed} \times R_{blowdown}) \quad (4)$$

Table 2: Equation factors data

Source/Utility	Factor/Rate	Description	Reference
Electricity (Malaysia Grid)	0.774 t CO_2e/MWh	CO_2 emission per MWh consumed	(Energy Commission, 2024)
Steam (Natural Gas)	0.0000564 t CO_2/MJ	CO_2 from steam generation using natural gas	(Marjanović and Mrzljak, 2021)
Steam enthalpy	2,750 MJ/t steam	Energy needed to generate 1 t of steam	(Marjanović and Mrzljak, 2021)
Steam Condensate Loss	20 % of steam used	Wastewater generated from unrecovered steam condensate	(Elwardany, 2024)
Cooling Water Blowdown	2 % of circulating water	Wastewater from cooling tower blowdown	(Elwardany, 2024)

2.4 Step 4: Construct the production pathways superstructure in P-graph

Next, the process network is built using the P-graph Studio software. Each pathway is represented as one operating unit (O-type node) in the P-graph superstructure, encompassing the full set of reactions and associated process parameters, while raw materials, intermediates, products, utilities, and wastes are represented as materials (M-type nodes). Connections between material and operating units are established by chemical reaction stoichiometric ratios and mass balances. For each node, the data is inputted, including flow rates, prices, emissions, and treatment costs. Figure 1 shows the generated pathways superstructure for the acrylic acid plant case study.

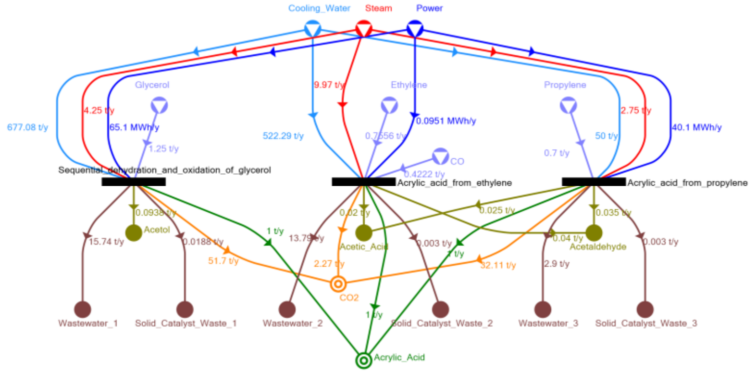

Figure 1: P-graph case study superstructure for acrylic acid plant

Both economic and environmental factors help in constraining the system and widening the analysis. The carbon tax cost is added at a rate of 7.8925 USD/t CO_{2e}, which makes P-graph select the most environmentally friendly route (Joshi, 2019). The summary of all case study data is presented in Table 3. It is worth highlighting that the consecutive data are arranged respectively in the table. The objective function of this optimization problem is to maximize the profit of the plant, and P-graph will select the highest profit route after constraining the system. The constraints and assumptions include fixed demand for acrylic acid (96,000 t/y), supply limits for each raw material, emission and waste penalties as cost factors. the Accelerated Branch and Bound (ABB) algorithm was used to find the optimal solution that maximizes the profit, P, while minimizing emissions and waste. The objective function of this superstructure is shown in Eq(5). It considers all the economic factors in the superstructure where $\mathrm{R}_{main\ product}$ is the main product's revenue, $\mathrm{R}_{byproduct}$ is the valuable byproducts' revenue, $\mathrm{C}_{raw\ materials}$ is the raw materials' cost, while converting the environmental factors into economic aspects where $\mathrm{C}_{utilities}$ is the utilities cost, Tax_{carbon} is the carbon tax, C_{waste} is the waste treatment cost, and $\mathrm{C}_{ww\ treatment}$ is the wastewater treatment cost.

Table 3: Case study data

Data/Information				Reference(s)
Main product		Acrylic Acid		
Market demand (t/y)		430,000 - 530,000		(Brown, n.d.)
Main product capacity (t/y)		96,000 (20 % or market demand)		
Selling price		1749.29 USD/t		(Puwar and Jalan, 2016)
Reaction routes	Acrylic acid from glycerol	Acrylic acid from ethylene	Acrylic acid from propylene	(Puwar and Jalan, 2016)
Raw material(s) needed	Glycerol	Ethylene, CO	Propylene	
Raw material(s) capacity (t/t acrylic acid)	1.25	0.7556, 0.4222	0.7	Stoichiometric ratios and calculations
Raw material(s) supply (t/y)	950,000	66,000,000, 400,000	63,000,000	(Glycerol market, 2024), (Huo, 2024), (Yingde Gases Group, 2025), (Argus Media, 2023)
Raw material(s) Price (USD/t)	816.33	613.07, 170.28	616.13	(Puwar and Jalan, 2016)
Byproduct(s) produced	Acetol	Acetic acid, Acetaldehyde	Acetic acid, Acetaldehyde	(Puwar and Jalan, 2016)
Byproduct(s) capacity (t/t acrylic acid)	0.09375	0.025, 0.035	0.025, 0.035	Stoichiometric ratios and calculations
Byproduct(s) price (USD/t)	1749.29	397.38, 877	397.38, 877	(Li et al., 2024), (Campos et al., 2014)
Waste produced		Solid Catalyst Waste		(Puwar and Jalan, 2016)
Waste capacity (t/t acrylic acid)	0.01875	0.003	0.003	(Puwar and Jalan, 2016)
Waste cost (USD/t)	-70,000	-7,750	-11,347	(IMARC Group, 2024)
CAPEX (USD)	95,600,000	560,000,000	221,500,000	(Sandid et al., 2023), (Campos et al., 2014)
OPEX (USD/y)	221,500,000	78,300,000	232,700,000	(Sandid et al., 2023), (Campos et al., 2014)
Utilities needed		Power, steam, and cooling water		
Utilities demand	65.10 MWh/t acrylic acid 4.25 t steam/t acrylic acid 677.08 t cooling water/t acrylic acid	0.0951 MWh/t acrylic acid 9.97 t steam/t acrylic acid 522.29 t cooling water /t acrylic acid	40.10 MWh/t acrylic acid 2.75 t steam/t acrylic acid 50.0 t cooling water/t acrylic acid	(Sandid et al., 2023), (Campos et al., 2014)
CO_2 production (t/t acrylic acid)	51.70	2.27	32.11	Stoichiometric ratios and calculations
CO_2 tax cost (USD/t CO_2e)		-7.8925		(Joshi, 2019)
Wastewater production (t/t acrylic acid)	15.74	13.79	2.90	Stoichiometric ratios and calculations
Wastewater treatment cost (USD/t wastewater)		-0.01188		(Pretel et al., 2014)

Objective Function: $\text{Max P} = \sum \text{R}_{main\ product} + \sum \text{R}_{byproduct} - \sum \text{C}_{raw\ materials} - \text{CAPEX} - \text{OPEX} - \sum \text{C}_{utilities} - \sum Tax_{carbon} - \sum \text{C}_{waste\ treatment} - \sum \text{C}_{ww\ treatment}$ (5)

3. Results and discussion

The P-graph optimization selected the ethylene route as the most economically and environmentally balanced pathway for acrylic acid production, yielding an annual profit of USD 25.9 M (Figure 2). This outcome was achieved using a composite single-objective function that integrates both economic and environmental factors by converting emissions and waste into cost penalties (e.g., carbon tax, wastewater treatment cost). This enables the model to capture trade-offs and rank feasible solutions beyond pure profit maximization.

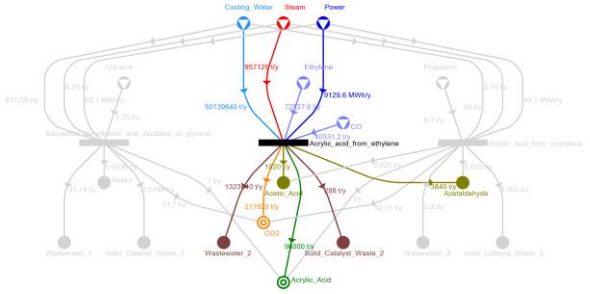

Figure 2: P-graph optimal solution for acrylic acid plant

A summary of the top-ranked solutions is provided in Table 4, showing both the P-graph output and EP values. The EP method (Seider et al., 2016) is commonly used for preliminary profitability screening and is calculated using Eq(6), where $\boldsymbol{S_{products}}$ is the product sales and $\mathbf{C}_{\boldsymbol{raw\ materials}}$ is the raw materials cost:

$$EP = \sum S_{products} - \sum \text{C}_{raw\ materials} \tag{6}$$

The P-graph solution prioritizes ethylene route due to its significantly better environmental profile, including lower CO_2 emissions (2.27 t/t) and wastewater generation (13.79 t/t) compared to propylene (32.11 t CO_2/t and 15.74 t wastewater/t) and glycerol (51.7 t CO_2/t and 2.90 t wastewater/t).

Table 4: P-graph result summary and economic potential for the acrylic acid pathways

Rank	Production Pathway	P-graph result (USD/y)	EP (USD/y)
1	Acrylic Acid from Ethylene	25,915,200.00	120,468,245.38
2	Acrylic Acid from Propylene	15,459,096.50	110,633,968.00
3	Sequential dehydration and oxidation of glycerol	13,235,882.00	85,715,850.00

While EP can provide an initial profitability screening, it neglects environmental challenges, utility use, CAPEX, and OPEX. For instance, although the propylene route shows a competitive EP value, it incurs higher OPEX (USD 232.7 M) and emissions, making it less favorable in a holistic context. Conversely, the ethylene route demonstrates strong performance across economic (moderate CAPEX: USD 560 M; OPEX: USD 78.3 M) and environmental metrics, justifying its selection. The results show that although the glycerol route offers the lowest wastewater generation (2.90 t/t), its extremely high CO_2 emissions (51.7 t/t) and low profitability (USD 13.2 M) placed it lowest in the ranking. This illustrates how the methodology accounts for trade-offs between different sustainability indicators and avoids biased conclusions based on isolated criteria.

4. Conclusions

This study demonstrated the benefit of the P-graph methodology for facilitating systematic decision-making in pathway selection and optimization in acrylic acid production. With the integration of economic and environmental considerations, this methodology provided a systematic way of identifying the most balanced and practical production route. In this case study, the ethylene route was selected, which addressed sustainability challenges and produced an estimated annual profit of USD 25.9 M. The analysis was based on literature-sourced data and assumed steady-state operation, which may not fully reflect real-world variability. Future research could explore integrating dynamic or plant-specific data, validating findings through experimental studies, and expanding the methodology to assess solution sensitivity under different sustainability priorities.

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