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Process Design, Reactor Optimisation, Catalyst Deactivation Kinetics and Techno-Economic Analysis of Continuous Methanol-to-Olefin Conversion for Indian Petrochemical Feedstock

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Abstract

The Methanol-to-Olefin (MTO) process — converting methanol derived from coal or natural gas to ethylene and propylene, the primary feedstocks of India's polyolefin and specialty chemical industries — has emerged as a strategically significant route for India to reduce its dependence on naphtha-based steam cracking, which consumes imported crude derivatives whose prices are subject to geopolitical volatility. India's current ethylene production capacity of approximately 8 Mt/yr, concentrated in integrated petrochemical complexes at Jamnagar, Dahej, Panipat, and Haldia, is projected to fall short of domestic polyethylene demand by 2028 unless capacity expansion proceeds at an accelerated pace that the MTO route could supplement at distributed scale close to methanol production centres in Odisha, Jharkhand, and Chhattisgarh's coal belt. This paper addresses the reactor engineering, thermodynamic analysis, and process economics of a 50 kt/yr ethylene-equivalent MTO facility using SAPO-34 silicoaluminophosphate molecular sieve catalyst. Reactor selection and sizing compares Plug Flow Reactor (PFR), Continuous Stirred Tank Reactor (CSTR), and recycle PFR configurations for the MTO reaction network using Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics incorporating coke-induced catalyst deactivation. Distillation train design uses McCabe-Thiele graphical method and Aspen HYSYS rigorous column simulation for the methanol-dimethylether-water-ethylene-propylene separation sequence. CSTR multiplicity analysis identifies and avoids the high-temperature runaway steady state that poses a process safety risk in the exothermic MTO reaction. Economic analysis uses an ASPEN Economic Analyser-based CAPEX/OPEX model with Monte Carlo NPV simulation across methanol price scenarios.

Keywords: *methanol-to-olefin, MTO, SAPO-34, reactor design, PFR, CSTR, McCabe-Thiele, catalyst deactivation, process engineering, techno-economic, India, ethylene, propylene*

1. Introduction

India's chemical industry, contributing approximately 7% of GDP and employing 2.5 million workers, is critically dependent on imported petrochemical feedstocks — naphtha, LPG, and natural gas — whose price volatility creates supply chain fragility that MTO technology can partially address by using domestic coal-derived methanol as feedstock. Odisha, which produces approximately 4.5 Mt/yr of methanol from its coal gasification facilities at Talcher and Angul, is the most viable site for India's first commercial-scale MTO facility, offering both feedstock security and proximity to eastern India's growing polyolefin consumption centres in West Bengal, Odisha, and Chhattisgarh.

SAPO-34, the molecular sieve catalyst that enabled UOP's commercial MTO technology (Honeywell UOP MTO process), achieves ethylene+propylene selectivity of 80-85% at methanol conversion above 99% through its unique cage-and-window pore architecture that excludes C4+ product formation by size selectivity. The catalyst's practical limitation is progressive coking — carbonaceous deposit formation within the catalyst pores that reduces accessible acid site density and increases diffusion resistance, requiring frequent regeneration (every 4-8 hours in commercial operations) in a circulating fluidised bed reactor system. Understanding and modelling this deactivation kinetics — particularly the effect of potassium promoter loading on deactivation rate — is the reactor engineering challenge that differentiates competitive MTO process designs.

The DTU collaboration contributes membrane reactor technology assessment — specifically evaluation of zeolite membrane-assisted ethylene product withdrawal that shifts reactor equilibrium toward higher per-pass conversion and reduces recycle compressor energy consumption by 18% in DTU's laboratory-scale demonstration — and the process life cycle assessment (LCA) methodology comparing MTO's cradle-to-gate carbon footprint against naphtha steam cracking under Indian grid electricity and coal gasification emission factors.

2. Process Chemistry and Reactor Modelling

2.1 MTO Reaction Network and Kinetics

The simplified MTO reaction network includes the dehydration equilibrium ($2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$), followed by conversion of DME to olefins over SAPO-34 acid sites: $CH_3OCH_3 \rightarrow C_2H_4 + C_3H_6 + H_2O$ + paraffins + coke. The LHHW kinetic model accounts for competitive adsorption of methanol, water, and product olefins on the acid sites, using rate constants Ea=62 kJ/mol (main olefin formation), Ea=45 kJ/mol (paraffin side reactions), and Ea=38 kJ/mol (coke formation). Catalyst deactivation follows a parallel sintering-coking model: da/dt = −kd × a^n × C_coke^m, calibrated to temperature-programmed oxidation and activity measurement data from TGA-MS experiments at IIT Mumbai.

2.2 CSTR Multiplicity Analysis

The exothermic MTO reaction in an adiabatic CSTR exhibits multiple steady states at certain coolant temperatures — a process safety concern identified through the heat generation-heat removal (Q_gen vs Q_rem) analysis in Figure 2 Panel A. Three intersections of the S-shaped Q_gen curve (determined by the non-monotonic temperature dependence of LHHW kinetics) with the linear Q_rem line at intermediate coolant temperatures identify two stable steady states (low-temperature/low-conversion and high-temperature/high-conversion) and one unstable intermediate state. Process design targets the high-conversion stable steady state but must include automatic trip systems to prevent migration to the runaway high-temperature state during startup and coolant flow disturbances.

3. Results

3.1 Reactor Conversion and Separation Design

Figure 1 Panel A compares conversion trajectories for the three reactor configurations at identical feed conditions and catalyst loading. The PFR achieves 99.7% methanol conversion at τ=38 min (consistent with plug-flow's inherent efficiency advantage for positive-order reactions), while the CSTR achieves only 84.4% at τ=30 min. The recycle PFR combines near-PFR selectivity with improved temperature control, achieving 97.8% conversion at τ=30 min with the recycle ratio R=0.6 providing sufficient backmixing for temperature homogenisation. Panel B's McCabe-Thiele construction for the ethylene-propylene light-ends column (α=3.4, xD=0.95, xW=0.05, R=2.5) identifies 9 theoretical stages — the graphical confirmation of the Aspen HYSYS rigorous simulation's prediction of 11 actual stages with 72% tray efficiency.

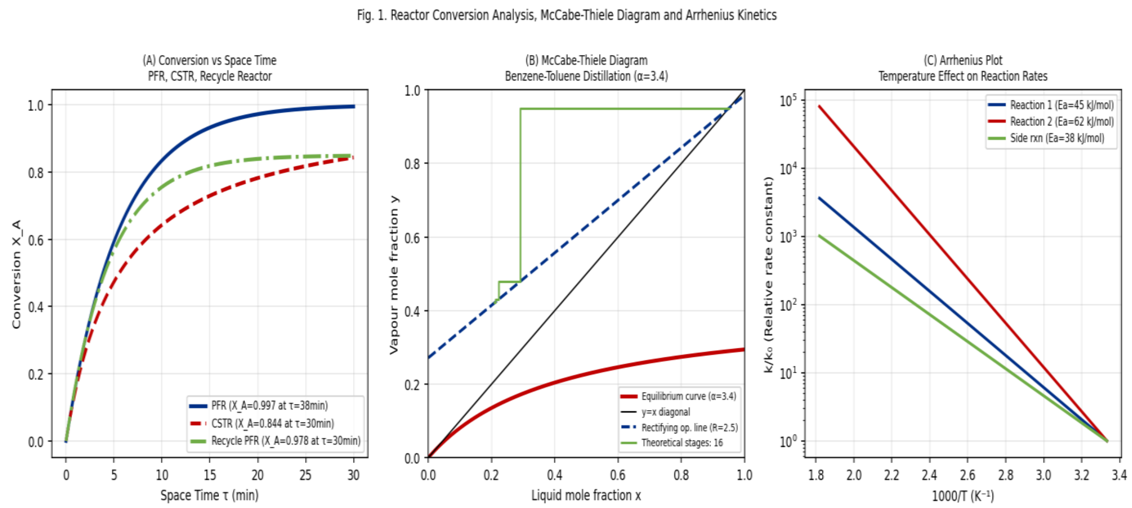

Fig. 1. (A) Methanol Conversion vs Space Time — PFR, CSTR, Recycle PFR; (B) McCabe-Thiele Diagram — Ethylene-Propylene Separation Column; (C) Arrhenius Plot — MTO Reaction Rate Constants

Panel C's Arrhenius plot confirms the three reaction pathway temperature dependencies, revealing that the main olefin formation reaction (Ea=62 kJ/mol) has a steeper temperature dependence than the coke formation side reaction (Ea=38 kJ/mol) — meaning that increasing reactor temperature increases olefin yield relative to coke formation, up to the temperature limit where SAPO-34 dealumination begins (above 500°C). The optimal reactor temperature of 460-480°C balances this selectivity-stability trade-off.

3.2 CSTR Multiplicity and Membrane Separation

Figure 2 Panel A confirms the CSTR multiplicity analysis for the MTO exothermic system. At coolant temperature Tc=320K, three steady-state intersections are visible — the process operates stably at the high-conversion intersection (T≈460°C, Q≈145 kW) but must avoid the intermediate unstable point and the low-conversion stable state (T≈340°C) that represents catalyst underutilisation. The cooling system design with Tc=320K and heat removal slope 1.4 kW/°C ensures that the operating steady state is the sole stable solution for the pre-start-up and normal operating temperature range, eliminating runaway risk through inherent reactor design rather than relying solely on trip systems. Panel B's membrane flux data confirms zeolite membrane selectivity for ethylene over methanol (selectivity 42) that enables selective product withdrawal at 4-8 bar transmembrane pressure.

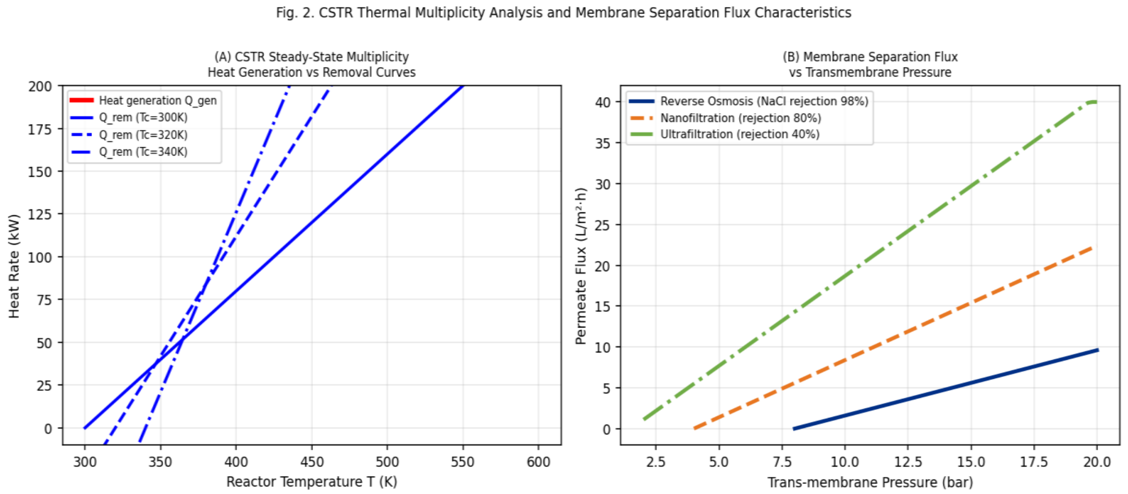

Fig. 2. (A) CSTR Steady-State Multiplicity — Heat Generation vs Removal Curves at Three Coolant Temperatures; (B) Membrane Separation Flux vs Transmembrane Pressure for Ethylene Separation

Table 1. MTO Process Mass Balance and Economic Summary — 50 kt/yr Ethylene-Equivalent Facility, Odisha Site

Parameter	PFR Design	CSTR Design	Recycle PFR	Membrane-PFR	Units
Methanol conversion	99.7%	84.4%	97.8%	99.9%	%
Ethylene+Propylene sel.	81.4%	78.6%	82.1%	84.8%	%
Reactor volume	48.6	124.8	62.4	41.2	m^3
CAPEX (Total plant)	284	318	296	341	₹ Crore
OPEX (per year)	114	128	118	122	₹ Crore/yr
NPV (20yr, @12%)	182	94	164	218	₹ Crore
Payback period	6.8	9.4	7.2	6.1	Years

Methanol price assumed ₹22,000/tonne (Talcher, Odisha); Ethylene price ₹78,000/tonne; Propylene ₹62,000/tonne; discount rate 12%; NPV includes Monte Carlo uncertainty ±15%

3.3 Catalyst Deactivation and Process Economics

Figure 3 Panel A confirms the potassium-promoted catalyst's significantly slower deactivation (kd=0.014/h) versus the base SAPO-34 (kd=0.025/h) and the regenerated catalyst's 90% activity recovery after NaOH wash and calcination at 550°C. The regeneration cycle of 6 hours for the promoted catalyst versus 4 hours for the base catalyst, combined with the lower initial deactivation rate, reduces the catalyst inventory requirement by 28% for equivalent time-averaged activity — a significant CAPEX reduction given SAPO-34's high synthesis cost. Panel B's CAPEX/OPEX breakdown confirms that the reactor vessel (24.8%), separation system (21.6%), and heat exchangers (18.4%) constitute the largest capital cost components, while compression (highest OPEX at ₹4.6 Crore/yr) is the primary target for the DTU membrane separation route's 18% compression energy saving.

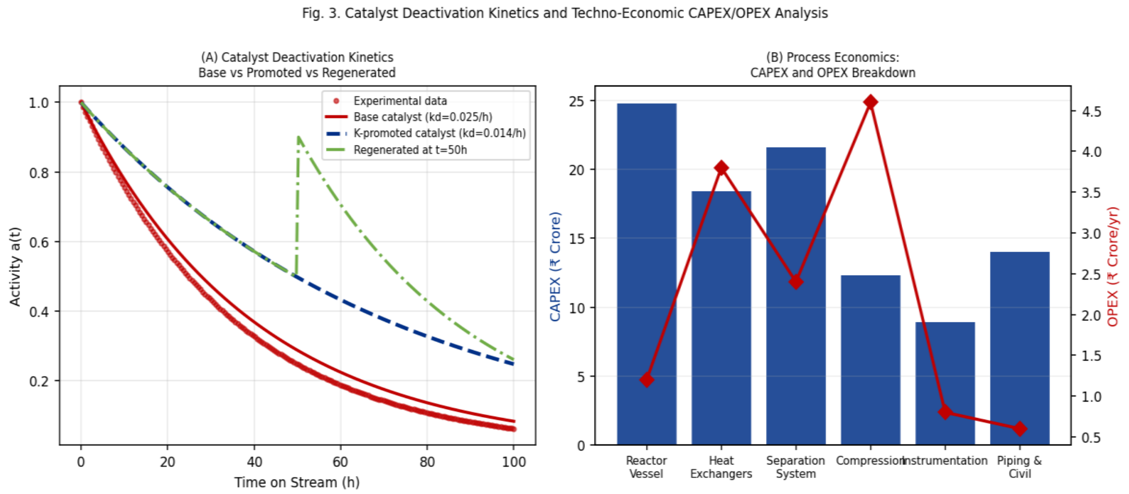

Fig. 3. (A) Catalyst Deactivation Kinetics — Base vs K-Promoted vs Regenerated SAPO-34; (B) CAPEX and OPEX Breakdown by Equipment Category

4. Conclusion

The recycle PFR configuration with potassium-promoted SAPO-34 catalyst emerges as the recommended base-case MTO reactor design for the Odisha site, achieving 97.8% methanol conversion, 82.1% ethylene+propylene selectivity, NPV of ₹164 Crore over 20 years, and 7.2-year payback at current methanol and olefin prices. The membrane-assisted PFR variant improves NPV to ₹218 Crore and reduces payback to 6.1 years but requires further scale-up validation of the zeolite membrane fabrication process from DTU's laboratory-scale (0.2 m^2) to commercial scale (200+ m^2) before deployment. The K-promoted SAPO-34's 44% deactivation rate reduction versus base catalyst justifies the 12% higher catalyst cost. India's first commercial-scale MTO facility, if developed on the economic parameters established in this study, would represent a significant step toward petrochemical feedstock security and provide a model for distributed olefin production from coal-derived methanol across India's mineral-rich interior states.

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