Low-Carbon Dimethyl Carbonate Design Under Utility and Carbon-Credit Uncertainty

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***Abstract*—Dimethyl carbonate (DMC) is a revealing case for low-carbon process design because phosgene-free routes involve different reaction equilibria, separations, utilities, feedstocks, and accounting boundaries. A configuration that is favorable under one electricity price or carbon-credit assumption can reverse rank when utility dispatch, capture attribution, co-product treatment, or catalyst life changes. This paper develops a process-superstructure and uncertainty-analysis method for comparing methanol oxidative carbonylation, direct synthesis from carbon dioxide and methanol, urea methanolysis, and carbonate transesterification. The method couples material and energy balances with discounted economics, explicitly bounded carbon accounting, and scenario-based robust optimization. Separate physical-carbon and financial-credit ledgers prevent double counting and reveal whether route rankings depend on policy treatment rather than process performance. Decision gates for chemistry, separations, product purity, and accounting produce an auditable basis for comparing feasible DMC configurations without collapsing multidimensional tradeoffs into one headline metric.**

***Index Terms*—dimethyl carbonate, process synthesis, carbon utilization, uncertainty, robust optimization, techno-economic analysis**

I. PROBLEM DEFINITION

DMC route selection is a coupled chemistry, separations, utilities, economics, and carbon-accounting problem. Reaction yields, kinetic parameters, capital factors, emission factors, and credit eligibility enter as traceable model inputs with stated units, conditions, sources, and uncertainty classes. This treatment makes route comparisons reproducible and prevents a favorable assumption in one ledger from being mistaken for a physical advantage in another.

The analysis identifies feasible DMC configurations whose cost and physical-inventory performance remain competitive across uncertainty in utilities, feedstocks, carbon intensity, catalyst life, and market conditions. DMC has multiple non-phosgene synthesis routes, including oxidative carbonylation, carbonate transesterification, urea methanolysis, and direct carbon-dioxide utilization [1], [2], [3]. The direct reaction of carbon dioxide with methanol is particularly instructive because thermodynamic equilibrium and water management complicate the apparently simple carbon-utilization narrative [2].

The framework evaluates route configurations rather than assigning an inherent "green" label to a reaction family. Environmental interpretation uses a declared functional unit, allocation rule, product boundary, and compatible lifecycle inventory. These elements connect directly to the physical ledger while remaining separate from financial credit treatment.

II. RELATED WORK AND MOTIVATION

DMC is a demanding route-selection problem because the routes differ before the reactor and after it. Oxidative carbonylation, carbonate transesterification, urea methanolysis, and direct carbon-dioxide conversion carry different co-reactants, equilibrium limits, water-management burdens, recycle structures, and impurities [1], [2], [3]. A route cannot be compared on a single reported conversion or selectivity value: separation duty, purge losses, catalyst replacement, and product specification can dominate the plant-level question. The direct CO_2 route makes the carbon feed especially visible while leaving thermodynamic and downstream burdens easy to understate. Process-synthesis literature provides the optimization vocabulary for choosing among coupled reactions, separations, and recycles [4], [5]. Green-chemistry work motivates transparent resource and waste accounting, but it also warns against reducing a multidimensional process to a single slogan or one mass-normalized metric [9]. Carbon-dioxide utilization research likewise distinguishes using CO_2 as a molecular feed from establishing a net climate benefit [8]. Product carbon-footprint guidance requires an explicit functional unit, boundary, inventory sources, and reporting treatment [7], [10]. The contribution is a route-comparison framework that keeps chemistry, physical inventory, and financial credit in separate ledgers until the reporting stage. A molecule of captured carbon in DMC product is a material-flow fact, while a credit depends on eligibility, ownership, verification, and a policy boundary. The superstructure identifies configurations whose ranking is robust to a disclosed set of assumptions and flags configurations whose appeal depends on an unsupported attribution or omitted separation burden. Figure 1 maps the route and accounting structure.

III. CANDIDATE ROUTE SUPERSTRUCTURE

A. Reaction Families

Let $r \in \mathcal{R}$ index route families. The baseline superstructure may contain the following reaction representations, subject to

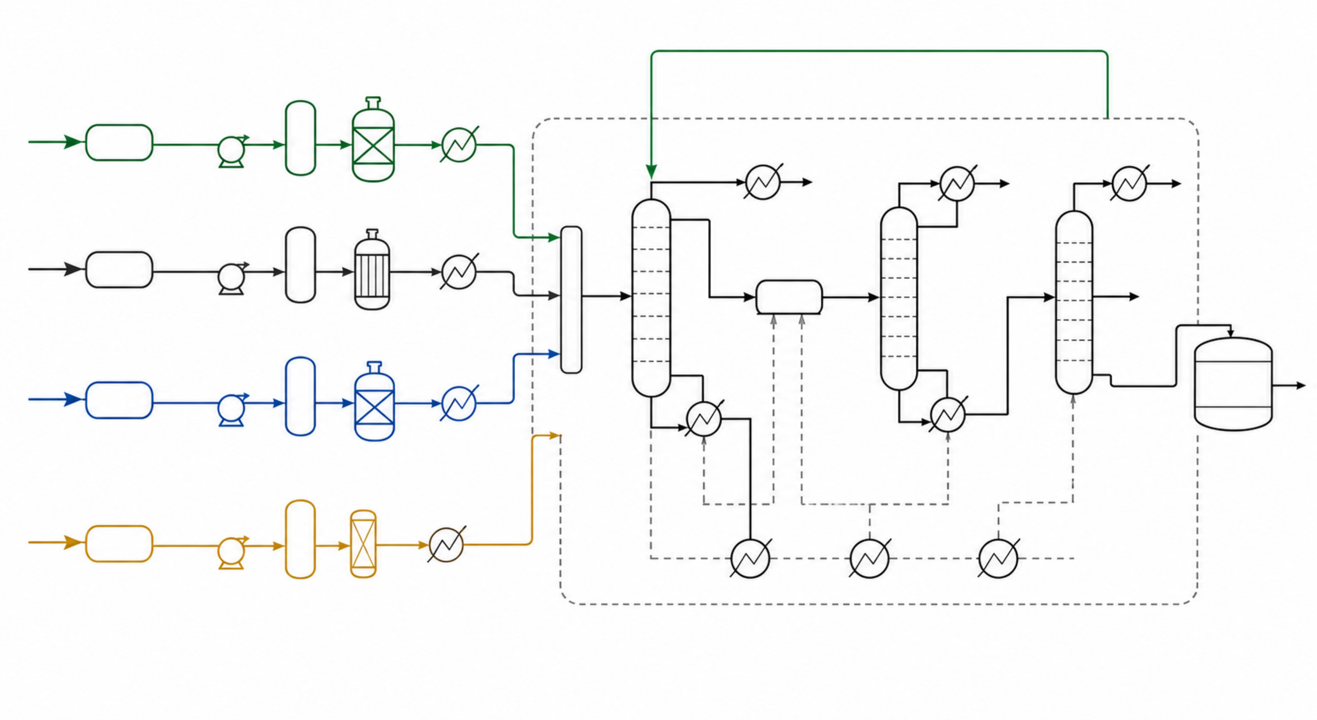

Fig. 1. DMC route-superstructure and accounting framework. Route branches share separation and recycle blocks while the dashed boundary separates material routing from carbon-accounting treatment.

sourceable catalyst and separation information:

$$2\mathrm{CH_3OH} + \mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \rightarrow (\mathrm{CH_3O})_2\mathrm{CO} + \mathrm{H_2O}, \tag{1}$$

$$2\mathrm{CH_3OH} + \mathrm{CO_2} \rightleftharpoons (\mathrm{CH_3O})_2\mathrm{CO} + \mathrm{H_2O}, \tag{2}$$

$$(\mathrm{NH_2})_2\mathrm{CO} + 2\mathrm{CH_3OH} \rightarrow (\mathrm{CH_3O})_2\mathrm{CO} + 2\mathrm{NH_3}. \tag{3}$$

Equation (1) is a stoichiometric representation of oxidative carbonylation, not a reactor design. Equation (2) is an equilibrium-limited reaction family, and Eq. (3) introduces ammonia management that must be represented in the downstream design. Carbonate transesterification is represented through its actual chosen carbonate intermediate rather than a generic conversion factor. The route set may be narrowed if public data cannot support a credible model for a given pathway.

Each route consists of reaction, phase separation, purification, recycle, utility, and waste-management blocks. A process configuration selects blocks through binary variables $y_j \in \{0, 1\}$; continuous variables f carry stream flows, temperatures, pressures, and duties. The purpose of a superstructure is to compare meaningful alternatives under common accounting rules, not to imply that all block combinations are physically or safely compatible.

B. Mass, Energy, and Purity Constraints

For every component i and unit j,

$$\sum_{s\in\mathrm{in}(j)} f_{i,s} - \sum_{s\in\mathrm{out}(j)} f_{i,s} + \nu_{ij}\xi_j = 0, \tag{4}$$

where ξ_j is reaction extent and ν_{ij} is the stoichiometric coefficient. Energy balances take the form

$$\sum_{s\in\mathrm{in}(j)} f_s h_s - \sum_{s\in\mathrm{out}(j)} f_s h_s + Q_j + W_j = 0. \tag{5}$$

Product qualification is represented explicitly. For example, a DMC product stream p must satisfy

$$\frac{f_{\mathrm{DMC},p}}{\sum_i f_{i,p}} \geq \overline{x}_{\mathrm{DMC}}, \tag{6}$$

with limits for water and route-specific contaminants defined by an intended use, not assumed from a generic market label. Separation-energy models must identify whether reflux, pressure, solvent recovery, and recycle compression are included. A yield alone is not a process design.

IV. Bounded Carbon and Economic Accounting

A. Physical Carbon Ledger

The physical carbon balance is reported independently of credits. For scenario ω, the modeled cradle-to-gate inventory is

$$I_{\mathrm{phys}}(y, f, \omega) = \sum_k a_k(y, f)\, g_k(\omega) + I_{\mathrm{direct}} - A_{\mathrm{co}}. \tag{7}$$

Here a_k is consumption of input or utility k, g_k is its documented inventory factor, I_{direct} contains direct releases, and A_{co} is a declared co-product allocation or system-expansion term. Units, temporal basis, and functional unit must be stated.

The default functional unit is one metric tonne of qualified DMC at the defined plant boundary.

Carbon entering as supplied CO_2 is tracked as a material flow but is not automatically treated as a negative emission. A separate fate vector records whether carbon is emitted, stored, transferred into product, or assigned to a co-product at the defined boundary. This prevents product-bound carbon and a capture credit from being counted twice.

B. Financial Ledger

The financial objective contains operating cost, annualized capital, revenues, and separately reported policy terms:

$$\begin{aligned} C_{\mathrm{ann}}(y,f,\omega) = \mathrm{CRF}\,K(y) + \sum_k p_k(\omega) a_k(y,f) \quad &(8)\\ + C_{\mathrm{catalyst}} + C_{\mathrm{waste}} - R_{\mathrm{product}} \quad &(9)\\ - R_{\mathrm{credit}}(\omega). \quad &(10)\end{aligned}$$

The capital-recovery factor is

$$\mathrm{CRF} = \frac{i(1+i)^n}{(1+i)^n - 1}, \tag{11}$$

for discount rate i and project life n. Credit revenue is permitted only when the credit regime, eligibility, verification, permanence, ownership, and non-overlap conditions are represented as explicit inputs. If those conditions are unknown, R_{credit} is set to zero in the base case and varied only in a labeled sensitivity case.

V. UNCERTAINTY-AWARE ROUTE SELECTION

A. Scenario Construction

Let $\omega \in \Omega$ contain electricity and thermal-utility prices, utility carbon intensities, methanol and carbon-feedstock prices, catalyst replacement interval, conversion/selectivity ranges, separation energy, plant capacity factor, and credit assumptions. The scenario ledger must distinguish three uncertainty types:

1) *Aleatory variability*, such as time-varying utility attributes;
2) *Epistemic uncertainty*, such as an immature catalyst-life estimate; and
3) *Policy ambiguity*, such as whether a credit may be claimed at the selected boundary.

These categories are not pooled blindly into a single Monte Carlo distribution. Epistemic and policy cases receive bounded stress tests and decision-contingent disclosure.

B. Robust Multi-Criterion Formulation

The primary optimization retains both cost and physical inventory:

$$\begin{aligned} \min_{y,f} \quad & \mathbb{E}_\omega\left[C_{\mathrm{ann}}(y,f,\omega)\right] + \lambda_C \mathrm{CVaR}_\alpha\left(C_{\mathrm{ann}}\right) && (12)\\ \min_{y,f} \quad & \mathbb{E}_\omega\left[I_{\mathrm{phys}}(y,f,\omega)\right] + \lambda_I \mathrm{CVaR}_\alpha\left(I_{\mathrm{phys}}\right) && (13)\\ \text{s.t.} \quad & \text{Eqs. (4)–(6); capacity and} && \\ & \text{route-compatibility constraints.} && (14)\end{aligned}$$

TABLE I

REQUIRED UNCERTAINTY CASES FOR EACH RETAINED ROUTE

Category	Required cases
Utilities	Low, central, high price; low, central, high marginal inventory; correlated price-inventory stress
Reaction and separation	Conversion/selectivity range, catalyst-life range, utility-duty range, recycle purge range
Economics	Capacity factor, capital contingency, product price, feedstock price, outage case
Carbon claims	No-credit base case; eligible-credit case; ineligible or double-count-risk case

The deliverable is a Pareto frontier plus a list of configurations dominated under every declared scenario, not one opaque weighted score. A scalar utility may be added for a specific decision meeting only after its weights and stakeholder authority are recorded.

VI. EVALUATION AND REPORTING FRAMEWORK

A. Model Hierarchy

Evaluation proceeds through four gates. First, pathways are screened using material and energy balances with transparent, literature-derived ranges. Second, route-specific separation and recycle models expose utility and purity bottlenecks. Third, independent mass- and elemental-balance checks establish carbon closure. Fourth, retained designs undergo uncertainty analysis and an external engineering review of plausibility. A route that cannot close the balances, meet purity under declared assumptions, or describe its carbon attribution is excluded from economic ranking.

Low-carbon interpretation depends on the functional unit, boundary, allocation method, electricity and thermal-utility assumptions, fate of carbon in product, and whether any credit is financial rather than physical. Carbon dioxide as a feed is therefore one physical-flow attribute rather than a sufficient classification.

B. Baselines

The minimum comparison set contains: (i) a documented commercial oxidative-carbonylation reference configuration, where inputs are sourceable; (ii) a direct-CO_2 configuration with water-management assumptions made explicit; and (iii) a route-neutral utility baseline that removes policy-credit terms. Route comparisons must expose their inventory assumptions and must not transfer a literature parameter into a new configuration without a documented validity check.

VII. PARAMETER PROVENANCE AND MODEL-DISCREPANCY PLAN

Parameter provenance is as important as the optimized flowsheet. Every reaction, separation, and utility parameter carries a source class: stoichiometric fact, peer-reviewed experiment, vendor or design estimate, public database factor, or analyst assumption. The register states the applicable temperature, pressure, feed composition, catalyst state, and unit basis. A value transferred across those conditions is treated

TABLE II
CORE OUTPUTS FOR ROUTE COMPARISON AND INTERPRETATION

Output	Interpretation
Mass and elemental closure	Model credibility prerequisite, not proof of commercial feasibility
Qualified-DMC yield	Route performance under the stated model and purity definition
Annualized cost range	Scenario-specific estimate, including disclosed exclusions
Physical inventory range	Boundary-dependent inventory, separate from financial credits
Rank stability	Fraction of stress cases preserving a pairwise route ordering
Dominance map	Configurations never preferred under declared objectives and scenarios

as an extrapolation and assigned a wider uncertainty range. The superstructure also distinguishes model discrepancy from ordinary scenario variation. A higher electricity price is a scenario change. An uncertain energy requirement because the separation model omits an azeotrope, heat integration, or solvent recovery is a model discrepancy. The latter cannot be handled merely by sampling a narrow price range; it triggers either a simplified but explicit bounding case or removal of the route from quantitative ranking until a suitable separation model is available. For transparency, each route is accompanied by a one-page assumption ledger covering reaction family and conversion basis, product specification, recycle and purge treatment, utility boundary, allocation rule, carbon-credit eligibility, capital-estimation class, and exclusions. The ledger appears beside each Pareto plot or ranking table. This practice is especially important for direct CO_2 routes, where an appealing carbon-flow diagram can obscure energy demand, water handling, or an unverified downstream claim.

VIII. DECISION GATES AND SENSITIVITY

Route screening begins with sourceable reaction stoichiometry, plausible operating conditions, and downstream separation logic. Each input is stored with a citation, unit, basis, date, range, and justification. An independent material-balance review checks elemental carbon, hydrogen, oxygen, and nitrogen closure before cost or inventory calculations enter the comparison. Three decision gates govern admission to uncertainty ranking. The chemistry gate rejects a route whose reaction and recycle model cannot close without unexplained loss or an undocumented dehydrating agent. The separations gate rejects a route that does not meet a declared DMC purity target under explicit utility and purge assumptions. The accounting gate rejects a negative-carbon or credit claim that cannot be tied to a stated product boundary and non-overlap rule. These gates focus the optimization on technically interpretable configurations. Rank reversal when credit revenue is removed, utility intensity changes over a defensible range, or water-removal duty increases identifies an assumption-sensitive decision. The result is represented through stability and dominance maps rather than one headline number. Kinetics, catalyst deactivation, materials compatibility, safety, and scale-up form additional evidence layers for field or pilot decisions.

IX. LIMITATIONS AND RESPONSIBLE INTERPRETATION

The superstructure approach complements catalyst experiments, corrosion assessment, hazardous-area design, relief analysis, and scale-up work. Equilibrium and kinetic parameters can be sparse or non-transferable across solvents, water activity, and reactor designs. Carbon accounting can also be structurally uncertain when captured-carbon ownership or downstream product fate is not established. Separating the physical ledger from the financial ledger provides a guardrail against unsupported environmental interpretation.

An economically unfavorable route under the selected assumptions may still have strategic value for feedstock security, technology learning, or policy reasons. Conversely, a favorable discounted-cost calculation is distinct from deployment maturity. The decision record therefore retains strategic value, technical readiness, and modeled economics as separate dimensions.

AUDIT AND REPRODUCIBILITY RECORD

A route-specific evidence register accompanies the executable model. The register identifies every reaction parameter, separation assumption, utility factor, capital factor, and allocation rule by source, unit, applicable conditions, and uncertainty class. Literature values include enough context to judge transferability: catalyst identity and state, solvent or dehydrating agent, pressure, temperature, feed composition, conversion basis, and product-purity basis. An untraceable value is not treated as a central estimate; it is either bounded explicitly or removed from the quantitative comparison. The accounting implementation preserves three linked but non-interchangeable tables. A material table traces elemental carbon from each feed through product, purge, direct release, and co-product streams. An inventory table maps utilities and feeds to the selected functional-unit boundary. A financial table records prices, capital recovery, product revenue, and any credit term. The model prohibits a credit from modifying the material table and flags a claimed negative inventory when the associated carbon fate, eligibility rule, and ownership condition have not been declared. For reproducibility, each route run emits a compact audit bundle: input-manifest hash, model revision, solver status, balance-closure results, purity check, active scenario, and all exclusion flags. Scenario summaries include the cases in which a route fails a chemistry, separation, or accounting gate rather than only a favorable average. This record makes it possible for a reviewer to identify whether a route preference follows from a robust process property or from a narrow price, credit, or boundary assumption.

X. CONCLUSION

This paper establishes a rigorous framework for comparing DMC process configurations under utility and carbon-credit uncertainty. Its central design choice preserves the distinction among chemistry, physical inventory, and financial-credit treatment. The superstructure, decision gates, Pareto analysis, and sourceable parameter ledger together make route rankings traceable to their technical and accounting assumptions.

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