E-ISSN: 2997-9382
American Journal of Technology Advancement
https://semantjournals.org/index.php/AJTA

| Research Article

Check for updates

Process Modeling and Thermal Analysis of Formaldehyde Reactors Cooled by Molten Salts and Dowtherm Oils: A Review

Yasmine Qais Hateem, Ala'a Abdulrazaq Al.mohammed
Department of chemical Engineering, college of Engineering, University of Basrah, Basra City, Iraq

Abstract

Formaldehyde is an industrial chemical of outstanding importance and is widely used in the manufacture of amino resins and other chemical derivatives. Industrial formaldehyde production is based primarily on the catalytic conversion of methanol in the gas phase, where two reactions occur simultaneously: the strongly exothermic oxidation of methanol to formaldehyde and the endothermic dehydrogenation of methanol, together constituting an autothermal reaction system. In industrial operation, formaldehyde synthesis via the excess air route is performed in multitubular catalytic reactors packed with iron–molybdenum-based metal oxide catalysts. Operation under these conditions allows high methanol conversion to be obtained at near-atmospheric pressure. Because the oxidation reaction is strongly exothermic, effective removal of the released heat is required in order to maintain stable reactor operation.

Heat is removed by circulating a heat-transfer medium on the shell side of the reactor, with molten salt systems and organic heat-transfer fluids, such as Dowtherm-based media, being commonly employed to control temperature profiles and suppress hot-spot formation.

After catalytic conversion, the formaldehyde-containing process gas is rapidly cooled and directed to absorption units, where formaldehyde is absorbed in water or urea solution to produce aqueous formaldehyde or urea–formaldehyde concentrate. Careful control of absorption conditions and reactant ratios is required to ensure product stability, solubility, and suitability for downstream fertilizer applications. The need for integrated and industrially calibrated reactor models for reliable comparison of cooling strategies is highlighted.

Keywords: Formaldehyde reactor; Urea–formaldehyde synthesis; Nitrate–nitrite molten salt; Dowtherm; Process modeling; Thermodynamic analysis.

This is an open-access article under the CC-BY 4.0 license

1. Introduction

Formaldehyde (FA, H_2CO) is the simplest aliphatic aldehyde and is present in nature at low concentrations. It is formed through metabolic processes in plants and animals, photochemical reactions in the atmosphere, and incomplete combustion processes [1]. Due to its high chemical reactivity, formaldehyde has become the most important aldehyde in industrial applications and is

widely used as a basic C1 building unit in the manufacture of many chemical products [2]. Pure formaldehyde is unstable and undergoes rapid polymerization, and for this reason it is commercially handled in aqueous form as formalin, which typically contains about 37 wt% formaldehyde and is stabilized by the addition of methanol [1]. A major fraction of global formaldehyde production is used in the manufacture of thermosetting resins, mainly urea–formaldehyde, phenol–formaldehyde, and melamine–formaldehyde resins. These materials are widely employed in wood-based construction products, adhesives, and plastics [3,4]. In addition to resin production, formaldehyde is utilized in several other industrial sectors, including automotive manufacturing, textile processing, energy-related applications, and antibacterial formulations [4].

In urea–formaldehyde resin manufacture, formaldehyde reacts with urea through condensation and polymerization reactions. The extent and progression of these reactions control the molecular structure of the resin and influence its performance during application [7,8]. Variations in formaldehyde concentration, operating temperature, and product stability have been shown to affect resin quality and subsequent processing behavior [8,9]. From an operational standpoint, the formaldehyde reactor located upstream in the process is required to deliver a product stream characterized by a stable composition and well-controlled thermal conditions [9,10].

Commercial formaldehyde production is mainly achieved through the catalytic conversion of methanol in the gas phase. Three industrial routes are commonly applied, namely the silver-catalyzed process, the BASF process, and the metal oxide-based Formox process [1]. Silver-catalyzed reactors are generally operated at relatively high temperatures and provide moderate methanol conversion. In comparison, the Formox process utilizes iron–molybdate catalysts and is operated at lower temperatures while achieving methanol conversions exceeding 99% together with high selectivity to formaldehyde [1,5]. Owing to these operating characteristics, the Formox route has been widely adopted and represents a significant share of the global formaldehyde production capacity [6].

In the Formox process, partial oxidation of methanol takes place in multitubular fixed-bed reactors under strongly exothermic conditions. After leaving the reactor, the product gas containing formaldehyde is routed to absorption units, where formaldehyde is absorbed in water, as illustrated schematically in Figure 1. Because methanol oxidation is associated with a high rate of heat release, efficient heat removal is required in order to maintain stable reactor operation, limit hot-spot formation, and preserve catalyst activity over extended operating periods. For this reason, industrial reactor designs incorporate external cooling systems, most commonly based on thermal oils or molten salt mixtures [5].

Accurate description of reactor behavior is therefore essential, particularly with respect to thermal effects. Axial temperature profiles along the reactor length exert a strong influence on methanol conversion, formaldehyde selectivity, and catalyst lifetime, and they are of central importance for achieving safe and stable operation in industrial formaldehyde production units [11,12].

The objective of this study is to develop a reactor model for comparing molten salt and Dowtherm cooling systems in industrial multitubular formaldehyde reactors.

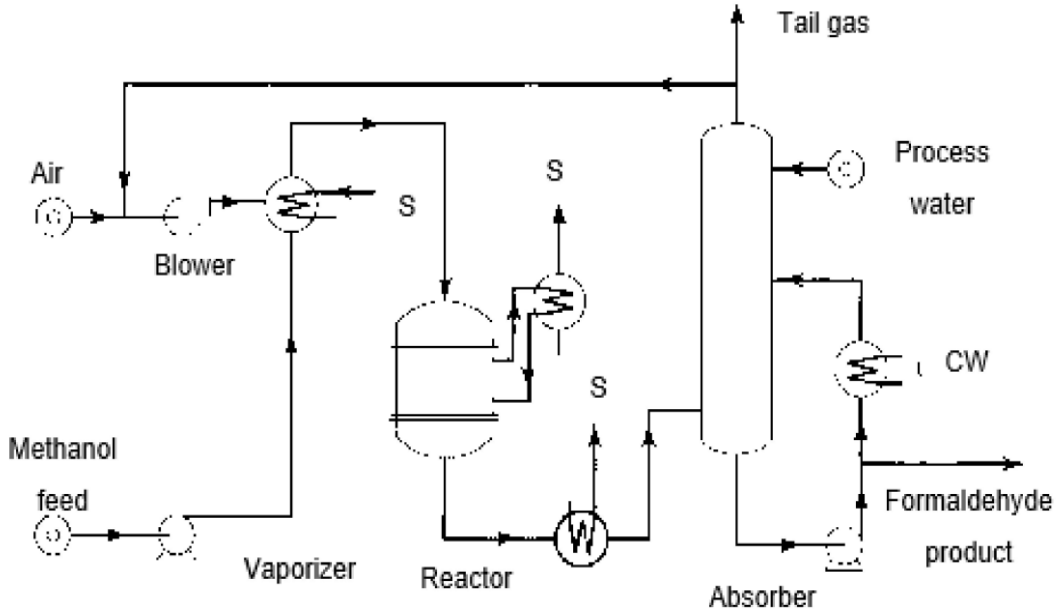

Figure 1. Process diagram of typical Formox process plant. S = steam; CW = cooling water. [5].

3. Multitubular Formaldehyde Reactor Modeling

Mathematical models developed for industrial multitubular fixed-bed formaldehyde reactors commonly adopt one-dimensional steady-state formulations along the axial coordinate [11,12]. These models typically incorporate component mass balances, an energy balance for the reacting gas phase, and pressure-drop correlations for flow through packed beds [12,16]. Reaction kinetics are generally expressed as functions of temperature and partial pressures, accounting for multiple parallel and consecutive reactions [10,17].

Thermal modeling plays a central role in these studies, as industrial formaldehyde reactors often exhibit pronounced hot-spot formation near the reactor inlet [13,14]. Accurate prediction of hot-spot magnitude and location is critical for evaluating reactor safety, thermal control efficiency, and catalyst lifetime [16,18]. These modeling approaches provide the foundation for evaluating the role of different cooling strategies , as schematically illustrated in Figure 2.

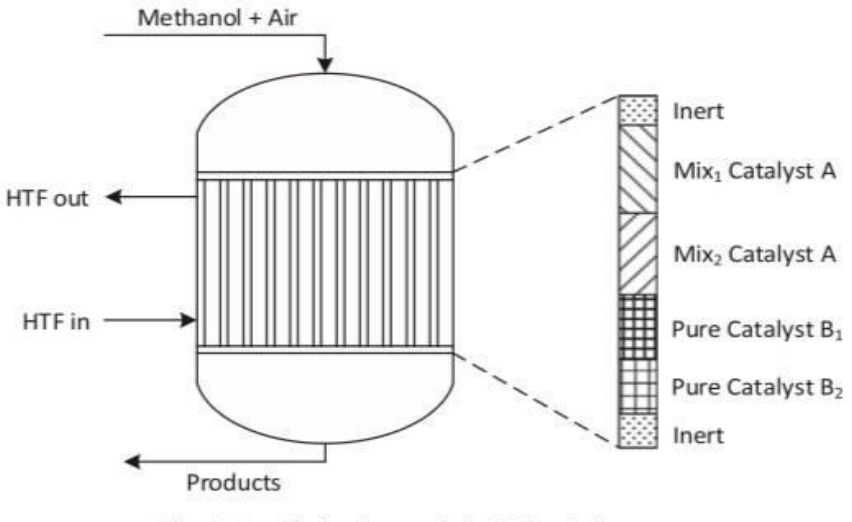

Figure 2. Schematic diagram of the industrial multitubular formaldehyde reactor [23].

4. Thermodynamic Characteristics of Cooling Media

4.1 Molten Salt

Molten nitrate–nitrite salt mixtures are extensively used as heat-transfer media in high-temperature industrial systems due to their high heat capacity, good thermal conductivity, and favorable thermal stability [19]. Compared with pure nitrate salts, nitrate–nitrite mixtures typically exhibit lower melting points, which makes them more suitable for continuous industrial operation.

In multitubular formaldehyde reactors, nitrate–nitrite molten salts enable efficient heat removal and improved temperature uniformity along the reactor length. These characteristics contribute to reduced temperature gradients and effective suppression of inlet hot spots, which is crucial for maintaining catalyst activity and reaction selectivity [19].

4.2 Dowtherm oil (an organic heat-transfer fluid)

Dowtherm oils are widely applied organic heat-transfer fluids characterized by ease of handling, relatively low pumping requirements, and good heat-transfer performance within moderate operating temperature ranges [15]. Dowtherm-based heat-transfer systems show limitations when applied under strongly exothermic reaction conditions. Their heat capacity is lower than that of molten salt systems, and their thermal stability is restricted at high temperatures [7,15]. Under similar feed rates and thermal loads, Dowtherm-cooled reactors have been reported to reach higher maximum operating temperatures compared with reactors cooled by molten salts [15]. At elevated temperatures, Dowtherm fluids may undergo thermal degradation and oxidation. Such behavior can lead to fouling and a gradual reduction in heat-transfer efficiency, which increases maintenance requirements during long-term operation. These factors impose practical limits on the maximum operating temperature of Dowtherm-cooled multitubular reactors, particularly at high space velocities [15].

5. Comparative Thermodynamic Performance

Studies reported in the literature indicate that molten salt cooling provides more effective thermal control than organic heat-transfer oils when reactors operate under high heat-release conditions [13,14,19]. Higher overall heat-transfer coefficients associated with molten salts result in more uniform axial temperature profiles, whereas Dowtherm-cooled reactors tend to approach their operating limits as thermal load increases [14,15].

Dowtherm cooling has nevertheless been applied within restricted operating ranges because of its simpler system configuration and ease of operation. Within these ranges, reactor models are commonly used to compare the performance of alternative cooling media and to define suitable operating windows for specific industrial reactor designs .To support these qualitative observations, a quantitative comparison of key thermal performance parameters reported in the literature is presented in Table 1:

Table 1. Quantitative comparison of Dowtherm cooling systems and molten salt for multitubular formaldehyde reactors

Parameter	Molten Salt Cooling Loop	Dowtherm Cooling Loop	Literature evidence
ΔT hot-spot (K)	40–80	90–160	Schotborgh et al. (2010); Tronconi et al. (2001)
Overall heat transfer coefficient, U ($W \cdot m^{-2} \cdot K^{-1}$)	1500–4000	300–800	Tronconi et al. (2001); Moustafa (2003)
Maximum tube wall	550–650	650–750	Moustafa (2003);

temperature, Twall,max (K)			Schotborgh et al. (2010)
Coolant specific heat capacity, Cp ($kJ \cdot kg^{-1} \cdot K^{-1}$)	1.3–1.6	0.9–1.1	Dowtherm datasheet; molten nitrate salts
Thermal stability limit (K)	>800	≈700	Dow Chemical; industrial practice
Axial temperature uniformity	High	Moderate	Stankiewicz & Eigenberger (1991)

6. Review of Previous Studies

The following section summarizes representative studies reported over the past decades, focusing on reactor modeling strategies, cooling media, and unresolved challenges.

6.1 Evolution of Kinetic and Reactor Modeling Approaches

Mars and van Krevelen (1954) proposed one of the earliest and most influential redox-type mechanisms for methanol oxidation over metal oxide catalysts. Their work established the fundamental role of lattice oxygen in oxidation reactions, forming the mechanistic basis for most subsequent kinetic models used in formaldehyde synthesis reactors [10]. Building on this mechanistic foundation, Dente and Collina (1966) simplified the complex reaction network by introducing a global kinetic model under steady-state and homogeneous assumptions. This approach enabled early reactor-scale modeling and demonstrated that overall reactor behavior could be reasonably captured using a limited number of dominant reactions [11]. With the increasing relevance of reactor-scale analysis for industrial design, Schwedock et al.(1989) examined methanol oxidation over iron–molybdenum catalysts using a simplified reactor model based on Arrhenius-type power-law kinetics. Their results showed that feed temperature has a strong influence on methanol conversion as well as formaldehyde selectivity. On this basis, the authors concluded that simplified kinetic formulations may be sufficient for engineering-level calculations under certain operating conditions [12]. In order to overcome the limitations associated with purely kinetic descriptions, more detailed reactor models were subsequently proposed. Moustafa (2003) developed a heterogeneous packed-bed reactor model in which intraparticle mass transfer was explicitly taken into account using a dusty gas formulation. Comparison of the model predictions with industrial operating data showed good agreement and confirmed that diffusion effects have a significant influence on temperature profiles and overall conversion under practical conditions [17]. Tesser et al. (2003) extended this approach by coupling reaction kinetics with internal mass and heat transfer within the catalyst pellets. Their analysis demonstrated that neglecting transport phenomena leads to appreciable errors in the prediction of reactor performance, especially in strongly exothermic reaction systems [20]. Studies focusing on intrinsic reaction kinetics were also reported. Deshmukh et al. (2005) investigated methanol oxidation over Fe–Mo catalysts under differential conditions in order to minimize transport limitations. Their work identified Langmuir–Hinshelwood reaction behavior and the presence of surface saturation and water inhibition effects, providing intrinsic kinetic parameters suitable for reactor modeling [21].Dynamic reactor behavior was addressed in later studies. Arreeyah and Kittisupakorn (2014) applied a dynamic plug-flow model to an adiabatic fixed-bed formaldehyde reactor operated with silver catalysts. Their simulations showed that formaldehyde yield reaches a maximum at an intermediate operating temperature and that water content affects hot-spot development [22]. Braz et al. (2019) presented a dynamic reactor model for an industrial multitubular system, including pressure drop, energy balances, and catalyst deactivation. Catalyst deactivation was related to cumulative methanol consumption, allowing prediction of long-term reactor behavior using industrial data [23]. Olatunde et al. (2021)

introduced a two-dimensional non-isothermal model that accounted for axial and radial temperature variations as well as wall heat losses. Their results showed that adsorption heat contributes to hot-spot formation and that simplified models underestimate maximum temperatures [24].At the catalyst scale, Bowker (2024) examined methanol oxidation over Fe–Mo catalysts and showed that catalyst surface structure and active-site distribution influence formaldehyde selectivity and stability under industrially relevant conditions [25]. In a broader context, D'Auria et al. (2025) reviewed the use of molten salt mixtures as energy carriers in thermochemical systems, highlighting their relevance for high-temperature heat-transfer applications [19]. More recently, Zakeri Gheshmi et al. (2025) developed a dynamic isothermal reactor model incorporating catalyst deactivation and industrial data to improve productivity and catalyst lifetime [26].

Table 2 summarizes representative studies published over the past decades, highlighting their focus, cooling medium, main achievements, and remaining limitations

Reference	Catalyst	Model Type	Cooling Strategy	Main Results
Mars & van Krevelen (1954)	Metal oxides	Redox reaction mechanism (MvK)	Not considered	Established the role of lattice oxygen in methanol oxidation and formed the mechanistic basis for later kinetic models.
Dente & Collina (1966)	Generic oxide catalyst	Global steady-state kinetic model	Not considered	Demonstrated that overall reactor behavior can be captured using simplified global kinetics.
Schwedock et al. (1989)	Fe–Mo	One-dimensional reactor model with power-law kinetics	Simplified cooling	Showed the strong influence of operating temperature on conversion and selectivity; highlighted thermal sensitivity of the reactor.
Moustafa (2003)	Fe–Mo	Heterogeneous packed-bed model including dusty gas formulation	External cooling (thermal fluid)	Demonstrated that intraparticle diffusion strongly affects temperature profiles and conversion; achieved good agreement with industrial data.
Tesser et al. (2003)	Fe–Mo	Coupled kinetic–transport reactor model	External cooling considered	Showed that neglecting transport phenomena leads to significant errors in reactor performance prediction.
Deshmukh et al. (2005)	Fe–Mo	Intrinsic kinetic model (Langmuir–Hinshelwood)	Not considered	Provided intrinsic kinetic parameters and identified surface saturation and water inhibition effects.
Arreeyah & Kittisupakorn	Ag	Dynamic plug-flow reactor model	Adiabatic (no cooling)	Identified an optimum reaction temperature and

(2014)		(adiabatic)		showed that water content suppresses hot-spot formation.
Braz et al. (2019)	Fe–Mo	Dynamic first-principles industrial reactor model	External cooling (heat-transfer fluid)	Successfully predicted long-term reactor behavior and hot-spot formation using industrial data.
Olatunde et al. (2021)	FeO/MoO_3	Two-dimensional non-isothermal reactor model	Wall heat losses included	Showed that adsorption heat contributes significantly to hot-spot formation; simplified models underpredict peak temperatures.
Inorganics study (2023)	Metal oxide catalysts	Mechanistic redox and surface analysis	Not considered	Clarified the role of surface oxygen species in methanol oxidation pathways.
Bowker (2024)	Fe–Mo	Mechanistic catalytic study (ensemble effects)	Not considered	Demonstrated that catalyst surface structure governs formaldehyde selectivity and stability.
Zakeri Gheshmi et al. (2025)	Fe–Mo	Dynamic reactor model with deactivation	Isothermal assumption	Showed that catalyst deactivation significantly affects long-term productivity and optimized operating conditions using industrial data.

As summarized in Table 2, show that most previous work has focused on reaction kinetics and reactor modeling, while thermal aspects have often been treated in a simplified manner. Only a few of the available studies address heat-transfer effects in sufficient detail, and validation against industrial data is not commonly reported. Moreover, the cooling medium itself is often treated as a secondary aspect rather than a defining parameter of reactor behavior. As a result, comparisons between different cooling options are usually indirect. This points to the need for reactor models capable of evaluating cooling strategies under operating conditions representative of industrial practice.

6.2. Influence of Operating Variables on Thermal Behavior and Selectivity

Several early investigations addressed the effect of operating conditions on methanol oxidation to formaldehyde. Gates et al. (1979) reported that higher reactor temperature increases methanol conversion but leads to a loss in selectivity because of side reactions. an increase in space velocity assists in achieving improved temperature control within the reactor [13]. The influence of reactor geometry and cooling configuration was examined by Stankiewicz and Eigenberger (1991). Their work showed that reactor thermal behavior is closely related to flow arrangement and coolant distribution, and that heat-removal efficiency as well as hot-spot sensitivity depend on reactor design parameters [14]. Comparable conclusions were reported by Reuss et al. (1998). Their study showed that deviations in operating pressure and feed composition favor the development of hot spots and accelerate catalyst deactivation in industrial reactor systems [9]. The role of heat-removal efficiency was examined in detail by Tronconi et al. (2001). They demonstrated that

inadequate cooling is associated with pronounced axial temperature gradients and unstable reactor behavior, while improved heat-transfer conditions lead to steadier operation and improved selectivity [16]. Hassan and Hummadi (2004) investigated the effect of reaction temperature and reported that formaldehyde yield increases with temperature up to an optimum value, beyond which selectivity decreases owing to the increasing contribution of side reactions [27].

Heat-transfer constraints in non-isothermal reactors were further analyzed by Schotborgh et al. (2015). Their results indicated that coolant flow configuration together with overall thermal resistance governs both the severity and axial location of hot spots in fixed-bed reactors [18]. The influence of enhanced heat and mass transfer was discussed by Sanz et al. (2011), who showed that the use of structured catalysts reduces temperature gradients and improves thermal stability under strongly exothermic operating conditions [24]. The effect of feed composition was examined by Khodakov et al. (2013). Their findings showed that although excess oxygen increases methanol conversion, it also markedly increases the tendency for hot-spot formation, thereby requiring careful control of the oxygen feed ratio [28].

Based on data obtained from an industrial formaldehyde production unit, Ghahraloud and Farsi (2017) reported that coolant inlet temperature is the primary variable controlling axial temperature profiles and overall reactor stability during operation [29]. More recent investigations have considered additional factors influencing reactor behavior. Pan et al. (2022) examined methanol oxidation over cobalt-based catalysts and reported that both reaction temperature and oxygen partial pressure affect formaldehyde selectivity, reflecting the influence of catalyst surface structure on reaction performance [25]. Geometric effects were addressed by George (2023), who showed that low tube-to-particle diameter ratios enhance wall effects and reduce radial heat-transfer efficiency, thereby promoting hot-spot formation [30]. Wang et al. (2023) reported that operation at elevated pressure leads to changes in kinetic behavior that are not adequately described by conventional models [31]. Finally, Deitermann et al. (2024) confirmed that accurate thermal control is required to maintain selectivity, particularly when catalyst surface properties interact strongly with temperature under industrial operating conditions [32].

Table 3. Summary of reported effects of operating parameters on methanol oxidation to formaldehyde

Study	Reactor Type	Catalyst	Key Operating Variables	Main Findings
Gates et al. (1979)	Fixed-bed reactor	Metal oxides	Temperature, pressure, space velocity	Increasing temperature enhances methanol conversion but decreases formaldehyde selectivity
Stankiewicz & Eigenberger (1991)	Multitubular fixed-bed reactor	—	Reactor geometry, coolant flow configuration	Reactor geometry and flow arrangement strongly influence heat-removal efficiency and hot-spot sensitivity
Reuss et al. (1998)	Industrial reactor	Fe–Mo	Temperature, pressure, feed ratio	Lower operating pressure favors selectivity; inadequate cooling promotes hot-spot formation
Tronconi et	Multitubular	Fe–Mo	Temperature, heat-	Enhanced heat removal

al. (2001)	fixed-bed reactor		removal efficiency	stabilizes reactor operation and improves thermal uniformity
Hassan & Hummadi (2004)	Laboratory tubular reactor	Fe–Mo	Reaction temperature	Optimum formaldehyde yield observed at approximately 300 °C
Schotborgh et al. (2010)	Multitubular fixed-bed reactor	Fe–Mo	Coolant flow configuration	Co-current cooling improves hot-spot control compared to counter-current operation
Sanz et al. (2011)	Structured fixed-bed reactor	Metal oxides	Reactor configuration, heat & mass transfer	Process intensification using structured catalysts improves heat and mass transfer, reducing temperature gradients and enhancing thermal stability
Khodakov et al. (2013)	Catalytic reactor	Metal oxides	Oxygen concentration	Excess oxygen increases hot-spot formation risk despite higher conversion
Ghahraloud & Farsi (2017)	Industrial multitubular reactor	Fe–Mo	Feed temperature, coolant temperature, air-to-methanol ratio	Coolant temperature is the dominant factor controlling reactor thermal behavior
Pan et al. (2022)	Catalytic reactor	Co-based	Temperature, O_2 partial pressure	Catalyst surface structure strongly affects formaldehyde selectivity
George et al. (2023)	Fixed-bed reactor	—	Reactor geometry (D/dp ratio)	Low D/dp ratios deteriorate radial heat transfer and promote hot-spot formation
Wang et al. (2023)	Jet-stirred reactor (gas-phase)	—	Pressure, temperature	High-pressure methanol oxidation exhibits distinct kinetic behavior, indicating limitations of conventional kinetic models
Deitermann et al. (2024)	Catalytic reactor	Metal oxide catalyst	Temperature	Precise thermal control is critical for maintaining selectivity due to strong temperature–surface structure interaction

As shown in Table 3 indicate that methanol oxidation reactor performance depends strongly on operating conditions, including reaction temperature, oxygen concentration, and cooling behavior. In particular, the results show that coolant temperature and the capacity for heat removal largely determine hot-spot formation and the associated loss of selectivity. These observations indicate that accurate thermal modeling is required to assess reactor behavior and to compare the performance of different cooling media under industrial operating conditions.

7. Research Gap and Novelty

A review of previous studies shows that most published work has treated formaldehyde reactor modeling and cooling media performance as separate subjects. Detailed reactor models have often been developed without a consistent evaluation of coolant thermophysical behavior, while studies focusing on cooling media have rarely been examined within a unified reactor modeling framework under comparable industrial operating conditions.

In the present work, an integrated reactor modeling approach is developed to allow direct comparison between nitrate–nitrite molten salt cooling and Dowtherm-based cooling systems. The model incorporates temperature-dependent coolant properties and enables quantitative analysis of axial temperature profiles and hot-spot formation, providing a consistent basis for evaluating thermal control strategies relevant to industrial urea–formaldehyde production.

8. Conclusions

Published studies examining multitubular fixed-bed formaldehyde reactors indicate that both nitrate–nitrite molten salts and Dowtherm heat-transfer oils have been applied as external cooling media. Reported results show that molten salt cooling systems provide more effective heat removal and lower hot-spot intensity, particularly in reactors operating under high heat-release conditions. Improved temperature uniformity associated with molten salt cooling contributes to enhanced thermal stability and safer industrial reactor operation.

Dowtherm-based cooling systems have been applied in a number of studies because of their relatively simple operation and ease of handling. Reported results show, however, that their lower heat capacity and limited thermal stability restrict performance when reactors are operated under high thermal loads. As a result, the use of Dowtherm cooling is constrained by the selected operating conditions and the allowable temperature range of the process.

While extensive work has been carried out on reaction kinetics and overall reactor behavior, many published models describe coolant-side heat transfer using simplified assumptions. Moreover, only a limited number of studies have performed direct and quantitative comparisons of different cooling media under consistent modeling conditions. These findings point to the value of reactor models that account for temperature-dependent coolant properties, detailed heat-transfer behavior, and representative industrial operating constraints when assessing cooling strategies for formaldehyde reactors in urea–formaldehyde production

References

1. Franz, A. W.; Kronemayer, H.; Pfeiffer, D.; Pilz, R. D.; Reuss, G.; Disteldorf, W.; Gamer, A. O.; Hilt, A. Formaldehyde. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons Inc.: Hoboken, NJ, USA, 2016; pp. 1–34.
2. Soares, A. P. V.; Portela, M. F.; Kiennemann, A. Methanol selective oxidation to formaldehyde over iron–molybdate catalysts. *Catal. Rev. Sci. Eng.* 2005, *47*, 125–174.
3. IHS Markit. Formaldehyde – Chemical Economics Handbook. Available online: https://www.ihs.com/products/formaldehyde-chemical-economics-handbook.html (accessed on 28 September 2017).

4. American Chemistry Council. Formaldehyde – Applications. Available online: https://formaldehyde.americanchemistry.com/Applications/ (accessed on 28 September 2017).
5. Gerberich, H. R.; Seaman, G. C. Formaldehyde. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2013; pp. 24–26.
6. Andersson, L.-O. New green policies in China. In *Informally Speaking: A Formaldehyde Magazine from Johnson Matthey*; Johnson Matthey: London, UK, 2019; pp. 12–13.
7. Urea–Formaldehyde Resins. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany.
8. Pizzi, A. *Wood Adhesives: Chemistry and Technology*; CRC Press: Boca Raton, FL, USA, 1983.
9. Reuss, G.; Disteldorf, W.; Gamer, A. O.; Hilt, A. Formaldehyde. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 1998.
10. Mars, P.; van Krevelen, D. W. Oxidation carried out by means of metal oxide catalysts. *Chem. Eng. Sci.* 1954, *3*, 41–59.
11. Dente, M.; Collina, A. A kinetic study of the catalytic oxidation of methanol. *Chem. Eng. Sci.* 1966, *21*, 1009–1016.
12. Schwedock, M. J.; Fogler, H. S.; Gates, B. C. Modeling of methanol oxidation to formaldehyde in fixed-bed reactors. *AIChE J.* 1989, *35*, 1237–1246.
13. Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, NY, USA, 1979.
14. Stankiewicz, A.; Eigenberger, G. Thermal behavior of multitubular fixed-bed reactors. *Chem. Eng. Sci.* 1991, *46*, 231–244.
15. Dow Chemical Company. DOWTHERM™ Heat Transfer Fluids – Technical Datasheet.
16. Tronconi, E.; Groppi, G.; Forzatti, P. Heat and mass transfer limitations in multitubular fixed-bed reactors. *Chem. Eng. Sci.* 2001, *56*, 653–663.
17. Moustafa, Y. M. Modeling and simulation of an industrial packed-bed formaldehyde reactor. *Chem. Eng. Process.* 2003, *42*, 817–827.
18. Schotborgh, W. O.; Nijhuis, T. A.; Kapteijn, F. Hot-spot formation and coolant flow effects in formaldehyde reactors. *Ind. Eng. Chem. Res.* 2010, *49*, 6682–6691.
19. D'Auria, L.; et al. Molten salt mixtures as heat-transfer media for high-temperature processes. *Renew. Sustain. Energy Rev.* 2025, *181*.
20. Tesser, R.; Salmi, T.; Santacesaria, E. Coupled kinetic–transport modeling of methanol oxidation in fixed-bed reactors. *Ind. Eng. Chem. Res.* 2003, *42* (9), 2067–2076.
21. Deshmukh, S. A. R. K.; van Sint Annaland, M.; Kuipers, J. A. M. Intrinsic kinetics of the partial oxidation of methanol over Fe–Mo catalysts. *Chem. Eng. J.* 2005, *109*, 87–96.
22. Arreeyah, M.; Kittisupakorn, P. Dynamic modeling and optimization of fixed-bed formaldehyde reactors. *Chem. Eng. Res. Des.* 2014, *92*, 2249–2260.
23. Braz, C. E. M.; Lima, E. L.; Pinto, J. C. Dynamic modeling and catalyst deactivation of an industrial multitubular formaldehyde reactor. *Chem. Eng. Sci.* 2019, *207*.
24. Olatunde, O. O.; et al. Two-dimensional non-isothermal modeling of formaldehyde synthesis reactors. *Chem. Eng. J.* 2021, *418*.

25. Hassan, A. A.; Hummadi, A. M. Effect of reaction temperature on formaldehyde yield in methanol oxidation reactors. *Chem. Eng. Process.* 2004.
26. Khodakov, A. Y.; et al. Effect of oxygen concentration on catalytic methanol oxidation and hot-spot formation. *Catal. Today* 2013.
27. Ghahraloud, H.; Farsi, M. Thermal behavior and operating parameter sensitivity of an industrial formaldehyde reactor. *Chem. Eng. Res. Des.* 2017.
28. George, S.; et al. Influence of tube-to-particle diameter ratio on heat transfer and hot-spot formation in fixed-bed reactors. *Chem. Eng. Sci.* 2023.
29. Wang, Y.; et al. High-pressure methanol oxidation: kinetic behavior and model limitations. *Combust. Flame* 2023.
30. Bowker, M. Structure sensitivity in methanol oxidation over iron–molybdenum oxide catalysts. *Catal. Today* 2024.
31. Zakeri Gheshmi, S.; et al. Dynamic isothermal reactor modeling and optimization of methanol oxidation with catalyst deactivation. *Chem. Eng. Res. Des.* 2025.
32. Deitermann, M.; et al. Temperature–structure interaction effects on selectivity in methanol oxidation over metal oxide catalysts. *Catal. Sci. Technol.* 2024