**Albahit Journal of Applied Sciences**
*"open-access, peer-reviewed biannual journal"*
*Volume 4, Issue 1, 2025*
*Page No: 94-102*
***Website***: *https://albahitjas.com.ly/index.php/albahit/en/index*

# Mathematical Modeling of Increasing Quenching on Methanol Production Rate for a Multi-Bed Quenching Reactor

**Ali Hamed [1*], Amira Mansour [2]**
[1,2] Chemical Engineering Department, Faculty of Engineering, University of Benghazi, Benghazi, Libya

[*]*Corresponding author:* ali.elhudhriy@uon.edu.ly

| Received: March 18, 2025 | Accepted: June 13, 2025 | Published: July 20, 2025 |
|---|---|---|

**Abstract:**
This research focuses on the importance of studying the effects of varying feed flow rates and quenching flow rates on methanol production rates and their impact on reactor bed temperatures. The primary objective is to determine the optimal conditions for achieving the highest methanol production rate. A mathematical model of the reactor was developed using the Graff kinetic model, incorporating hydrogenation reaction pathways for carbon monoxide and carbon dioxide, as well as the water-gas shift reaction. Differential equations for molar and energy balances were numerically solved using the Runge-Kutta method implemented in MATLAB. The results revealed that increasing quenching to 65% of feed reduced methanol production by 12%. In contrast, at quenching rate of 79% led to an increase in methanol production from 842 mol/s to 894 mol/s, representing a 6% improvement. These findings indicate that increasing the quenching flow rate positively impacts reaction temperatures and enhances methanol production, while reducing the feed flow rate can have adverse effects.

**Keywords**: Mathematical modeling, kinetic model, quenching rector, numerical analysis method, Matlab software.

# النمذجة الرياضية لدراسة تأثير تغير معدل التدفق على إنتاج الميثانول للمفعل تبريد متعدد الطبقات

**على حامد [1*]، أميرة منصور[2]**
[2،1] قسم هندسة الكيميائية، كلية الهندسة، جامعة بنغازي، ليبيا.

**الملخص**
من هذا البحث يتم التركيز على أهمية دراسة تأثير تغيير معدل تدفق التغذية ومعدل التدفق المستخدم في الطلقات الباردة (التبريد السريع) على معدل إنتاج الميثانول وتأثيره على درجات حرارة السرير لتحقيق الهدف المتمثل في تحديد أعلى معدل لإنتاج الميثانول. من خلال النمذجة الرياضية للمفاعل، باستخدام نموذج جراف الحركي ومسارات تفاعل الهدرجة لأحادي أكسيد الكربون وثاني أكسيد الكربون، بالإضافة إلى تفاعل تحويل الغاز إلى ماء. تم استخدام جميع هذه البيانات لحل المعادلات التفاضلية عدديًا لتحقيق توازن المول والطاقة باستخدام الحل العددي المطبق عبر طريقة رانج-كوتا المنفذة في MATLAB. من النتائج التي تم الحصول عليها، أدى التغيير الأول في التدفق إلى تقليل معدل إنتاج الميثانول بنسبة 12%. على العكس، تم ملاحظة أعلى إنتاج للميثانول في التغيير الثاني، حيث زاد إنتاج الميثانول من 842 مول/ثانية إلى 894 مول/ثانية، مما يشير إلى تحسن بنسبة 6% في إنتاج الميثانول. من النتائج، نستنتج أن زيادة معدل تدفق التبريد تؤثر على درجات حرارة التفاعل وتزيد من معدل إنتاج الميثانول بينما تقلل من معدل تدفق التغذية.

**الكلمات المفتاحية:** النمذجة الرياضية، النموذج الحركي، مفاعل التبريد، تحليل طرق العددية، برنامج ماتلاب FPGA.

## Introduction

Methanol is one of the most critical commodities in industrial chemistry, with over 90 production plants worldwide boasting a combined production capacity of 110 million metric tons (Mt). According to the Integrated Health System (IHS), global methanol demand reached 70 Mt in 2015, reflecting a staggering 500% increase over the past 15 years (Vincenzo Palma et al., 2018). This growth underscores methanol's importance as a versatile chemical feedstock and fuel additive in modern industrial applications.

The commercial-scale production of methanol dates back to 1923 when Badische Anilin-und-Soda-Fabrik (BASF) introduced the first high-pressure synthesis process. This method utilized a zinc oxide/chromium oxide catalyst to convert carbon oxides and hydrogen into methanol at pressures exceeding 300 bar and temperatures ranging from 350 to 400°C. However, the high-pressure process faced significant challenges, including excessive energy consumption per ton of methanol and limitations on scalability. Decades later, in 1966, Imperial Chemical Industries (ICI) revolutionized methanol production by developing a low-pressure methanol process (LPM). This innovation employed copper/zinc-based catalysts operating at pressures below 100 bar and temperatures between 200 and 300°C, significantly improving efficiency and reducing costs (Lee, 1989).

Today, various reactor conFigure urations are used in industrial methanol synthesis, with fixed-bed reactors—either with quench systems or multi-tubular designs with cooling—being the most prevalent. These reactors are typically modeled using commercial $CuO/ZnO/Al_2O_3$ catalysts (Leonzio, 2020). Recent studies have focused on optimizing methanol synthesis through advanced modeling and simulation techniques. For instance, Stoica et al. (2015) conducted a study to model, estimate, and optimize an adiabatic methanol synthesis reactor, aiming to maximize productivity while accounting for catalyst deactivation. Key decision variables included inlet temperature and composition, feed flow rate, and coolant temperature. Similarly, Leonzio (2020)

described a steady-state reactor model based on molar balances, where equations were derived with respect to catalyst weight or reactor length and solved numerically using MATLAB software. The primary objective of this paper is to determine the optimal conditions for maximizing methanol production by analyzing the effects of varying feed and quenching distributions on reaction temperatures within the reactor beds. By addressing these factors, this study aims to contribute to the ongoing efforts to enhance the efficiency and sustainability of methanol synthesis processes.

## Methodology

### Quenching Reactor.

ICI Technology

The quenching reactor modeled here is based on ICI technology (AI-Arifi, et al., 2015), as illustrated in Figure ures 1and 2 in addition to and table 1**(Bisotti,et al., 2022)**. The reactor is a multi-bed adiabatic reactor. The reactor contains five catalytic beds separated by four levels of cold shot gas distributors. These distributors comprise lozenges which surround and support the distribution pipes through Steady State temperature of the reacting mixture. The distributors are positioned across the full diameter of the reactor and are designed to give good mixing between cold shot and hot gas. They are spaced to allow free passage of the catalyst pellets during catalyst loading and unloading, thus allowing catalyst changes to be made with a minimum of down-time.

### Feed distribution scenarios:

In this study five scenarios for feed distribution between the quenching and non-quenching section of the reactor are to be investigated:

| (Base case) /Scenario | % of Feed in Non-Quenching Bed | % of Feed in Quenching Beds |
|---|---|---|
| a | 40 | 60 |
| b | 35 | 65 |
| c | 30 | 70 |
| d | 25 | 75 |
| e | 20 | 80 |
| f | 21 | 79 |

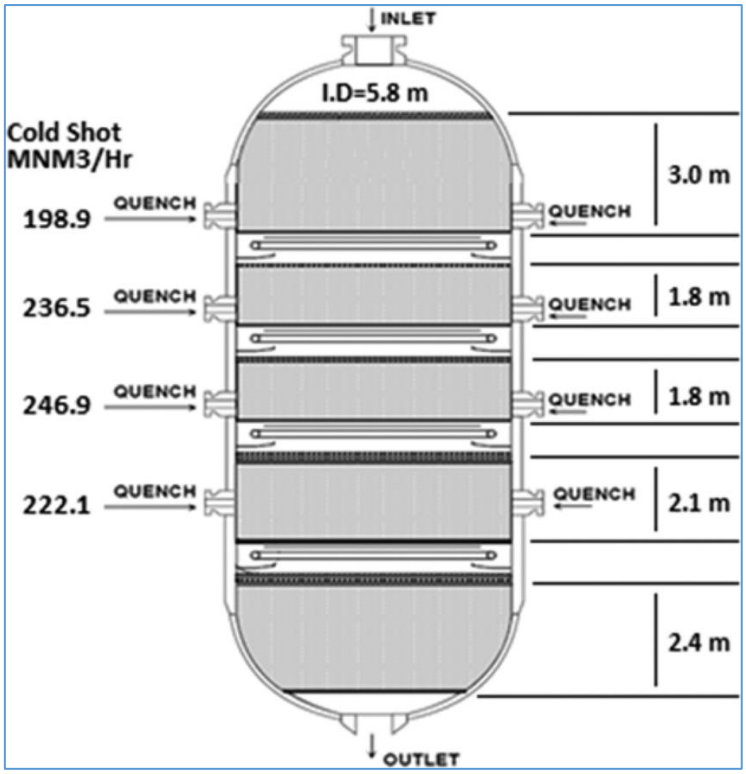



**Figure . 1**. Layout of ICI low pressure quench reactor (AI-Arifi, et al., 2015)

**Table .1.** ICI Design Case Data (Bisotti,et al., 2022).

| Parameter | Value |
|---|---|
| **Inlet flow (SYNGAS IN) ($Nm^3/h$)** | 567.1 |
| **Inlet Temperature °*K*** | 505.6 |
| **Inlet Pressure (bar)** | 96.85 |
| **Cold Shot Flow ($Nm^3/h$)** | |
| **Cold Shot 1** | 198.9 |
| **Cold Shot 2** | 236.5 |
| **Cold Shot 3** | 246.9 |
| **Cold Shot 4** | 222.1 |
| **Cold Shot Temperature ℃** | 83 |
| **Cold Shots and Inlet Flow (SYNGAS IN) Molar Composition (mol %)** | |
| **MeOH** | 0.422 |
| **$CO_2$** | 3.501 |
| **CO** | 4.645 |
| **$H_2$** | 78.5 |
| **$H_2O$** | 0.048 |
| **$CH_4$** | 10.39 |
| **$N_2$** | 2.394 |

Figure ure 2 reports feed distribution to both quenching and non- quenching beds of the reactor as well as percent distribution of cold shots among the four quench beds.

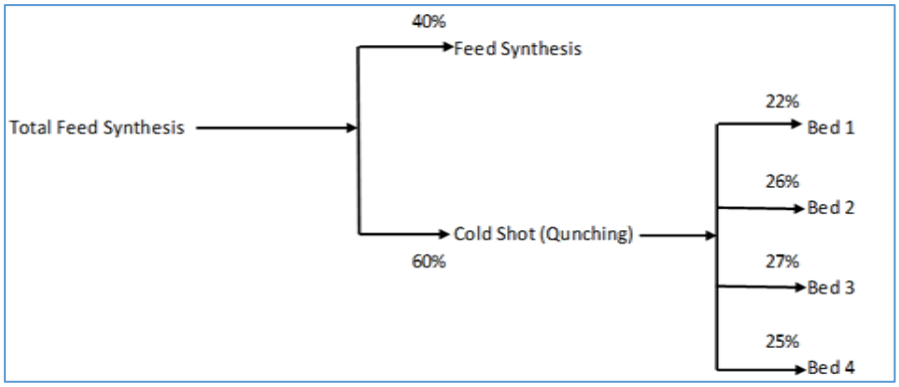



**Figure .2.** Chart of percentage inputs flowrate for ICI design.

**Methanol Synthesis**

The process of methanol synthesis over catalysts normally proceeds through three parallel reactions: CO2 hydrogenation, reverse water gas shift (RWGS) reaction, and CO hydrogenation. These reactions are shown below (Graff et, at,. 1988) :

$$CO + 2H_2 \rightleftharpoons CH_3OH \quad \Delta H_R^O = -91\ KJ.mol^{-1}$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H_R^O = -41KJ.mol^{-1}$$
$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad \Delta H_R^O = -50\ KJ.mol^{-1}$$

**Reactor modelling**

The simple PBR model was taken from a textbook by Scott Fogler. (2004), for multi reaction and one dimensional mathematical modelling of the synthesis

BR reactor is based on the following set of balance equations gas phase:

Mole balance:

$$\frac{dF_i}{dW} = \sum r_i \qquad (1)$$

Energy balance:

$$\frac{dT}{dW} = \frac{\sum -\Delta H_{Ri} * r_i}{\sum F_i * C_{Pi}} \qquad (2)$$

| | |
|---|---|
| $F_i$ | Molar flow rate of i components mol/s |
| $W$ | Mass of catalyst kg |
| $T$ | Temperature K |
| $r_i$ | The reaction rate of I components mol/kg s |
| $\Delta H_{Ri}$ | Heat of reaction of i reaction J/mol |
| $C_{Pi}$ | Specific heat coefficient at a constant pressure J/mol .K |

In this study it was considered a methanol synthesis process carried out over a commercial Cu/ZnO/Al2O3 catalyst. The kinetic model developed by Graaf ,et al. (1988).

$$r_{co2/MeOH} = \frac{k_1 K_{co2}\left(f_{CO2} f_{H2}^{1.5} - \frac{f_{MeOH} f_{H2O}}{f_{H2}^{1.5} K_{eqco2}}\right)}{(1 + K_{co} f_{co} + K_{co2} f_{co2})\left(f^{0.5} + \left(\frac{K_{H2O}}{K_{H2}^{0.5}}\right).f_{H2O}\right)} \qquad (3)$$

$$r_{RWGS} = \frac{k_2 K_{co2}\left(f_{CO2} f_{H2}^{1.5} - \frac{f_{H2} f_{co}}{K_{eqRWGS}}\right)}{(1 + K_{co} f_{co} + K_{co2} f_{co2})\left(f^{0.5} + \left(\frac{K_{H2O}}{K_{H2}^{0.5}}\right).f_{H2O}\right)} \qquad (4)$$

$$r_{CO/MeOH} = \frac{k_3 K_{co}\left(f_{CO} f_{H2}^{1.5} - \frac{f_{MeOH}}{f_{H2}^{1.5} K_{eqco}}\right)}{(1 + K_{co} f_{co} + K_{co2} f_{co2})\left(f^{0.5} + \left(\frac{K_{H2O}}{K_{H2}^{0.5}}\right).f_{H2O}\right)} \qquad (5)$$

Original Kinetic and Thermodynamic Parameters for the Considered Kinetic (Bisotti et, al,.2022):

A- kinetic coefficients:

$$k_1 = 1.09 * 10^5 e^{(-87500/RT)} \quad (6)$$

$$k_2 = 9.64 * 10^{11} e^{(-152900/RT)} \quad (7)$$

$$k_3 = 4.89 * 10^7 e^{\left(-\frac{11300}{RT}\right)} \quad (8)$$

B- Adsorption constants

$$K_{co2} = 7.05 * 10^{-7} e^{\left(\frac{61700}{RT}\right)} \quad (9)$$

$$K_{co} = 2.16 * 10^{-5} e^{(46800/RT)} \quad (10)$$

$$K_{H2O/H2^{0.5}} = 6.37 * 10^{-9} e^{\left(\frac{84000}{RT}\right)} \quad (11)$$

C- Equilibrium constants

$$\log_{10} K_{eqCO2} = \frac{3066}{T} - 10.592 \quad (12)$$

$$\log_{10} K_{eqRWGS} = \frac{-2073}{T} + 2.092 \quad (13)$$

$$\log_{10} K_{eqCO} = \frac{5139}{T} - 12.621 \quad (14)$$

Activation energy are expressed in J/mol, T in K. Fugacity for ideal gas assumed partial pressure P in bar.

**Mathematical modelling**

MATLAB is a software that uses an extremely effective and interactive language, which is widely used in several applications in engineering, especially aimed at numerical calculation. Integrating the technical computation for calculation with matrices, elaboration of graphs, numerical analysis, besides signal processing and algorithm development. There are many variants of the Runge-Kutta methods, ode45 is based on an explicit Runge-Kutta. That means the numerical solver ode45 combines a fourth order method and a fifth order method, both of which are similar to the classical fourth order Runge-Kutta (RK) method (Yong et, al,. 2021)

Figure ure 3 represents the flow chart used to carry out process simulations in MATLAB using the same assumptions of the ICI model. The developed program reproduced published data for the base case of 40/60 distribution.

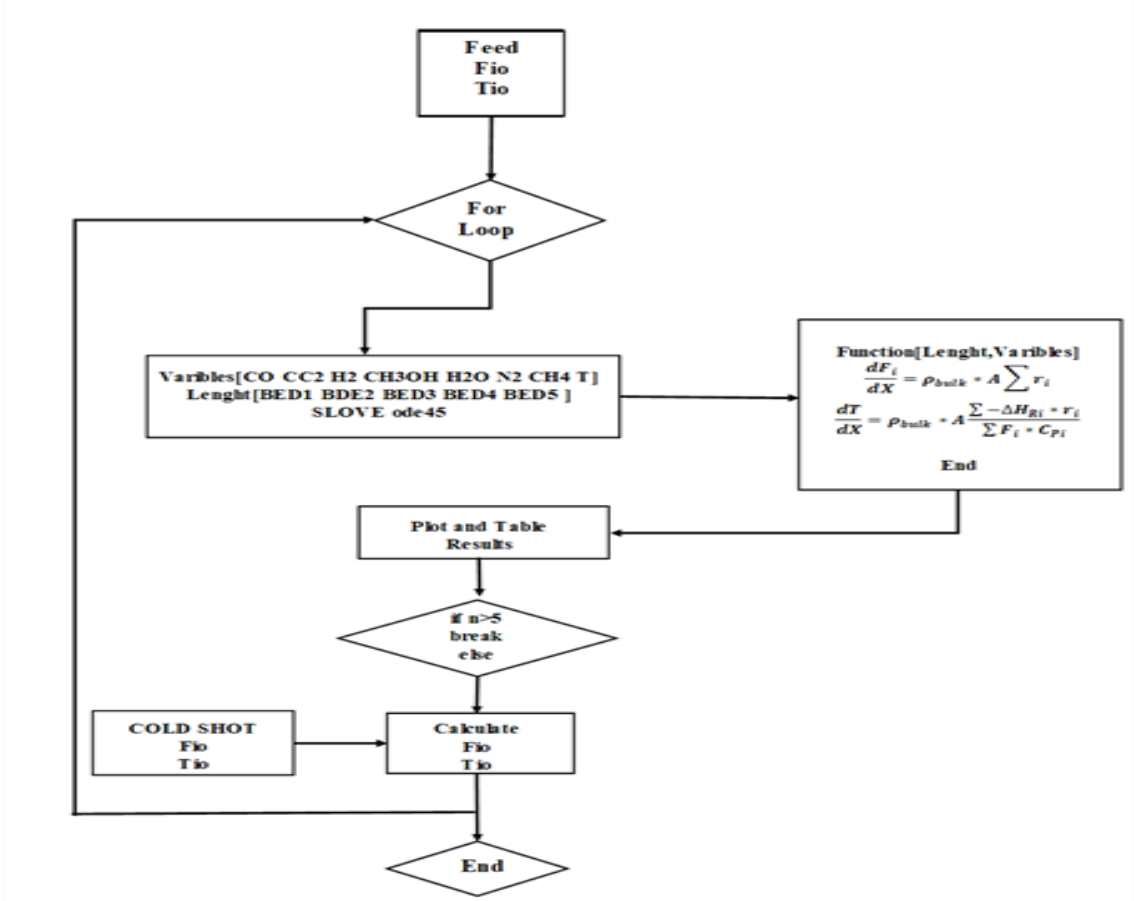



**Figure .3.** Flowchart mathematical modeling calculation by MATLAB software.

**Modeling Results:**

Figure ure 4 shows the predicted temperature distribution along reactor length using ICI design data (case a) as well as the case

where the percent of the feed used for cold shots is increased by 5 %(case b). As expected, the temperature profile for case b is below that for case a.

On the other hand as in Figure ure 5, the exit molar flow rate of methanol in case b is 842 mole/s higher than base case a indicating the validity of increasing percentage of cold shots to increase methanol production.

.

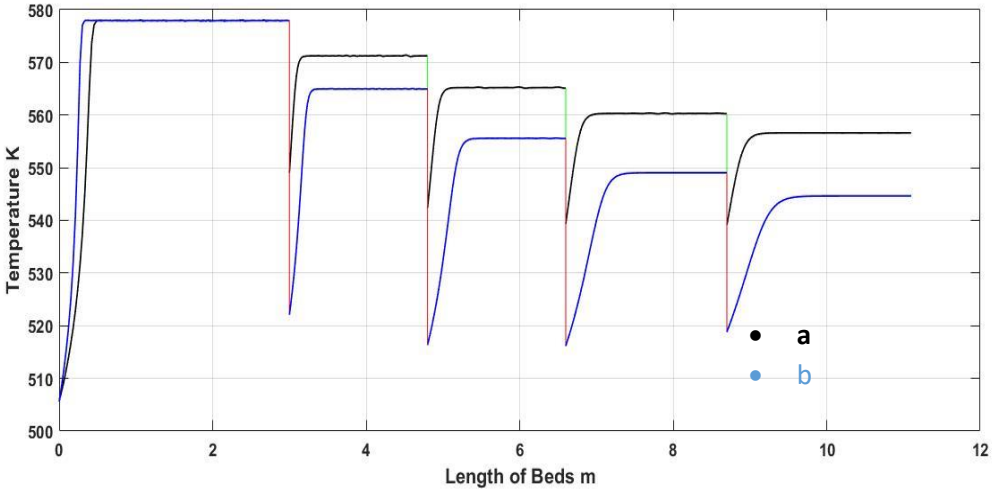



**Figure .4.** Temperature profile versus length of beds results mathematical modeling (a) design and (b)first changing.

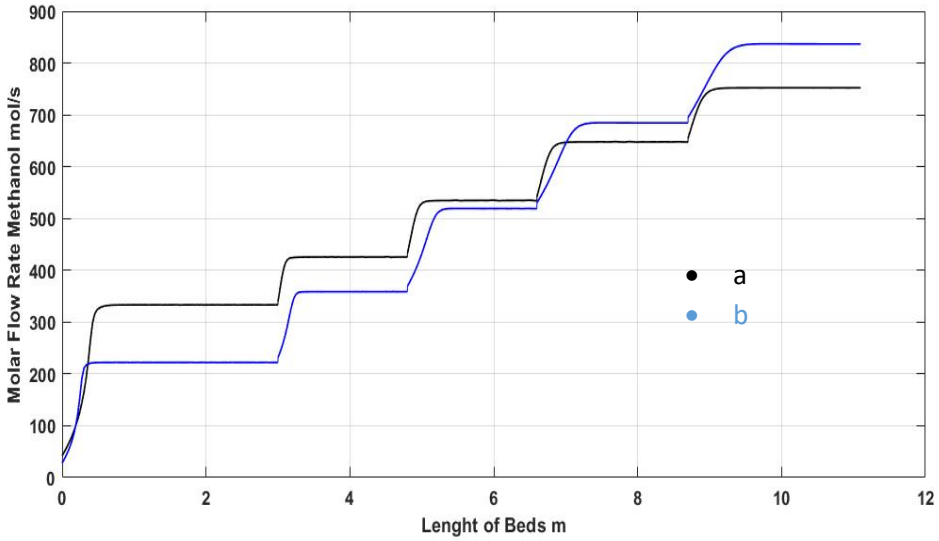



**Figure .5.** Methanol flow rate versus length of beds results mathematical modeling (a) design data (b) first changing.

As discussed in the methodology the percentage of feed used as cooled shots was increased in 5% increments from 60 to 80% and finally to79% which yielded optimum methanol production rate of 894 mole/s.

Figure ure 6 shows he predicted methanol molar flow rate along reactor length for all

Programmed scenarios. Figure ure 7 shows the predicted temperature distribution along reactor beds for all scenarios(a,b,c,d,e).

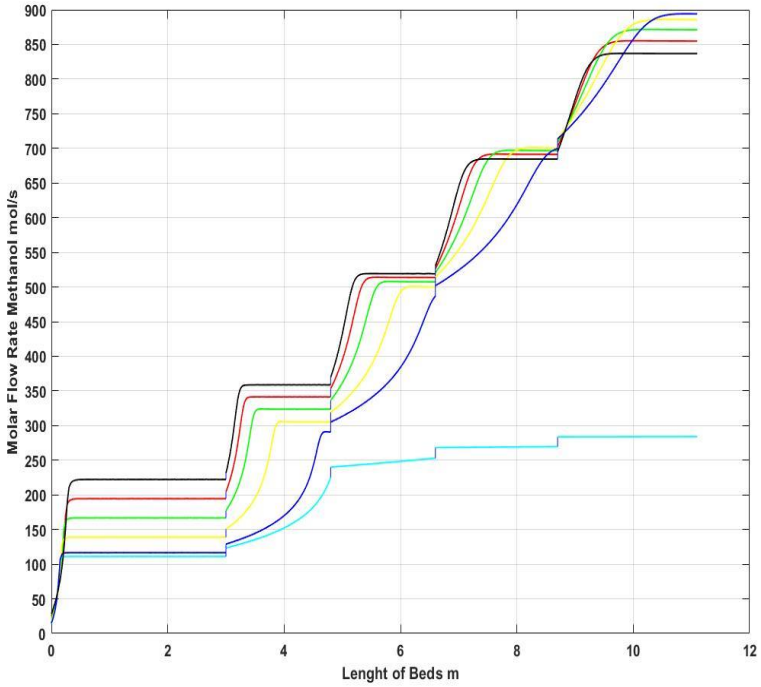
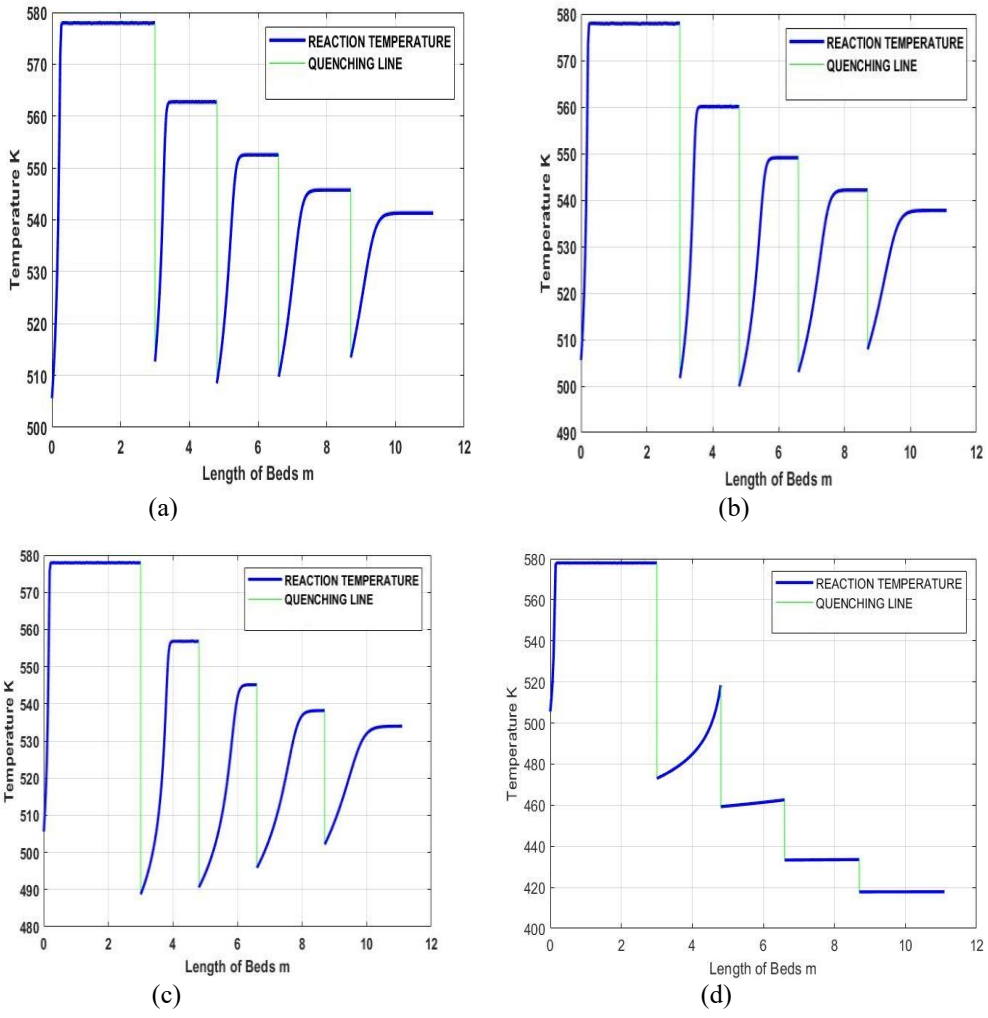
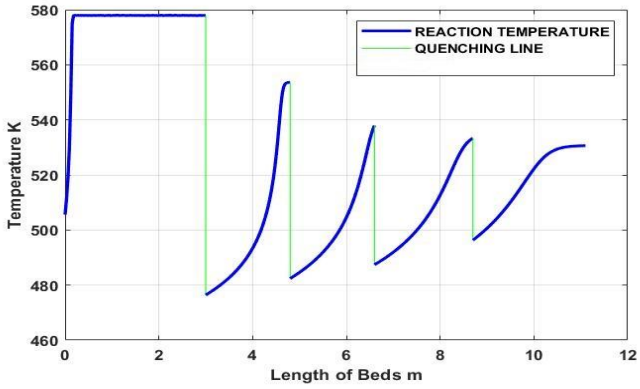



**Figure .6.** Methanol flow rate versus length of beds results mathematical modeling different mole flow rate between feed synthesis and cold shot (a) 40%-60% (b) 35%-65% (c) 30%-70%(d) 25%-75%(e) 20%-80% (f) 21%-79%.





(e)

**Discussion of Results:**

Through this work concluded the importance of studying effect changing flow rates that increasing the quenching flow rate and reducing the feed flow rate inlet the first bed improves methanol production due to the lower input temperatures of the remaining beds after mixing with the quenching. This improvement in production reached approximately 6%.

However, increasing the quenching flow rate has a certain limit, as when it reached 80%, the increase in the flow rate of methanol production in the beds was very minimal according to Figure ure 6 and 7(d) due to the inlet temperature of the second bed after mixing with cooling, which reached about 473 and had a downward effect on the rest of the beds. This is consistent with the study by Al-Fadhli et al. (1995) where the decrease in the inlet temperature to 488 affected the inlet temperatures of the other beds. Finally, From the results of previous attempts, it was concluded that the input temperatures determine the best rate for methanol production when the quenching flow rate reaches 79%.

**Conclusion:**

The results of this study demonstrate that increasing the quenching flow rate in a multi-bed adiabatic methanol reactor enhances methanol production by lowering the inlet temperatures of subsequent catalytic beds, thereby creating more favorable reaction conditions. The modeling showed that when the quenching flow rate was increased to 79% of the feed, methanol production improved by approximately 6%, rising from 842 mol/s to 894 mol/s, which highlights the significance of optimal feed distribution between quenching and non-quenching sections. However, further increases in quenching beyond this point produced minimal additional benefits due to excessively low inlet temperatures, which negatively affected the downstream catalytic beds. This finding confirms that there is an optimal operating window for quenching, beyond which performance gains diminish. Overall, the study concludes that careful adjustment of feed and quenching distributions is crucial for maximizing methanol yield, and that operating near a 21%/79% distribution between non-quenching and quenching sections provides the most efficient and sustainable production performance, in line with previous literature emphasizing the critical role of inlet temperatures in methanol synthesis.

**Recommendations**

1. **Operational Optimization**
   Industrial methanol plants using ICI-based quenching reactors should consider operating around a **21% feed in the non-quenching bed and 79% in quenching beds**, as this distribution maximizes production without overcooling.
2. **Process Control Strategies**
   Future plant design and operation should incorporate **advanced control systems** that dynamically adjust quenching flow based on real-time bed temperature profiles, ensuring optimal conditions are maintained across varying loads.
3. **Further Research**
   **Experimental Validation:** Pilot-scale experiments are recommended to validate the mathematical model and account for catalyst deactivation effects.
   **Economic Assessment:** A techno-economic analysis should be conducted to evaluate cost benefits of operating at 79% quenching versus other distributions.
   **Alternative Kinetic Models:** Incorporating more recent kinetic models (e.g., Nestler et al., 2020) may refine predictive accuracy.

4. **Sustainability Considerations**
   Improving methanol yield with optimal quenching reduces energy consumption per ton of methanol produced, contributing to **more sustainable and cost-effective methanol synthesis**.

**References**


Alarifi, A., Alsobhi, S., Elkamel, A., & Croiset, E. (2015). Multiobjective optimization of methanol synthesis loop from synthesis gas via a multibed adiabatic reactor with additional interstage CO2 quenching. Energy & Fuels, 29(2), 530-537.

Al-Fadli, A. M., Soliman, M. A., & Froment, G. F. (1995). Steady state simulation of a multi-bed adiabatic reactor for methanol production. Journal of King Saud University-Engineering Sciences, 7, 101-132.

Bisotti, F., Fedeli, M., Prifti, K., Galeazzi, A., Dell'Angelo, A., & Manenti, F. (2022). Impact of kinetic models on methanol synthesis reactor predictions: in silico assessment and comparison with industrial data. Industrial & Engineering Chemistry Research, 61(5), 2206-2226.

Graaf, G. H., Stamhuis, E. J., & Beenackers, A. A. C. M. (1988). Kinetics of low-pressure methanol synthesis. Chemical Engineering Science, 43(12), 3185-3195.

H.S. Fogler. (2004). Elements of Chemical Reaction Engineering, 4th ed., New Jersey, USA, Prentice Hall: Upper Saddle River, New Jersey, USA,.

Lee, S. (1989). Methanol synthesis technology.

Leonzio, G. (2020). Mathematical modeling of a methanol reactor by using different kinetic models. Journal of Industrial and Engineering Chemistry, 85, 130-140.

Nestler, F., Schütze, A. R., Ouda, M., Hadrich, M. J., Schaadt, A., Bajohr, S., & Kolb, T. (2020). Kinetic modelling of methanol synthesis over commercial catalysts: A critical assessment. Chemical Engineering Journal, 394, 124881.

Palma, V., Meloni, E., Ruocco, C., Martino, M., & Ricca, A. (2018). State of the art of conventional reactors for methanol production. Methanol, 29-51.

Stoica, I., Banu, I., Bobarnac, I., & Bozga, G. (2015). Optimization of a methanol synthesis reactor. UPB Scientific Bulletin, Series B: Chemistry and Materials Science, 77(4), 134-146.

Young, T., & Mohlenkamp, M. J. (2021). Introduction to numerical methods and Matlab Programming for Engineers.