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Noreen, A., Creaser, D., Pajalic, O. et al (2026). A review of pentaerythritol Synthesis; industrial manufacturing and separation processes. Journal of Industrial and Engineering Chemistry, 159: 15-23. http://dx.doi.org/10.1016/j.jiec.2025.12.017

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Journal of Industrial and Engineering Chemistry 159 (2026) 15–23

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Review Article

A review of pentaerythritol Synthesis; industrial manufacturing and separation processes

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ARTICLE INFO

Keywords:
Pentaerythritol
Synthesis processes
Separation processes
Homogeneous catalysts
Aldol condensation reaction
Cannizzaro reaction

ABSTRACT

Pentaerythritol (penta) is a versatile substance that has been used in manufacturing industries for decades as a starting material to produce various end products, including plastics, medicines, lubricants, paints, polymer cross-linking agents, and many others. Numerous patents have been published worldwide for penta synthesis to improve its industrial production. The synthesis and purification of penta are highly sensitive processes, making it challenging to achieve a high yield and adding significant complexity to the overall process. To date, no review has summarized the inventions aimed at improving the penta synthesis. This review compiles key research findings on synthesizing penta with high yields, minimizing waste production, and using efficient separation technologies. The effect of reactant ratios, amount of water, reaction temperature, and catalysts on penta synthesis is also summarized in the review. Based on literature analysis, the review offers suggestions and recommendations to pursue future research to improve penta synthesis processes further.

Introduction

Pentaerythritol (penta) is a versatile polyalcohol which serves as a fundamental building block for various applications in industries. The versatility in application of penta comes mostly from its tetraols as the four hydrogen atoms attached to each of its –OH groups can be substituted to other ions of interest [1–4]. Moreover, the four –OH groups attached to each terminal carbon can also be replaced by halogen-based substituents such as iodide or methyl bromide, which later can be replaced by different nucleophiles such as dimethyl amine or cyanides that are used as cationic surfactants [5–7]. Penta has nowadays gained popularity as a key ingredient for producing resins to make plastics, paints, cosmetics, oil additives, and various other commercial products [8–15]. Due to its multifaceted properties, penta has gained increasing prominence and its preparation has been patented by many companies and industries. Penta is generally produced when formaldehyde reacts with acetaldehyde in an alkaline medium (e.g. KOH, NaOH, $Ca(OH)_2$), most commonly NaOH, under controlled conditions as shown in Scheme 1. In the reaction mixture, formaldehyde and acetaldehyde initially undergo three sequential cross-aldol condensation reactions to give an intermediate called pentaerythrose which later reacts further with formaldehyde through a Cannizzaro reaction to give the final product penta [16].

With more detail, in the first cross-condensation reaction step, formaldehyde reacts with acetaldehyde to give rise to 3-hydroxypropional (3-HPA), see Scheme 2. This reaction occurs due to the presence of "acid" hydrogen on the α-carbon of acetaldehyde. Firstly, acetaldehyde forms a carbanion in the presence of a base which reacts with formaldehyde to form 3-HPA. This intermediate further reacts with formaldehyde to form 2-hydroxymethyl-3-hydroxypropanal and subsequently converts to 3-hydroxy-2,2-bis(hydroxymethyl)propionaldehyde. This final condensation product 3-hydroxy-2,2-bis(hydroxymethyl)propionaldehyde, also denoted pentaerythrose finally undergoes a Cannizzaro reaction in the presence of formaldehyde and NaOH to give penta as shown in Scheme 2.

Besides this main reaction, there are various side reactions that can also take place in the reaction mixture [18–21]. The reaction system is extraordinarily complex in terms of mechanism and kinetics. Several

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https://doi.org/10.1016/j.jiec.2025.12.017
Received 12 August 2025; Received in revised form 29 November 2025; Accepted 11 December 2025
Available online 11 December 2025
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other by-products are also produced during the self-condensation of formaldehyde and acetaldehyde [16,22–24]. Along with the desired penta formation in the Cannizzaro reaction, formaldehyde reacts with sodium of the alkaline catalyst to form sodium formate salt and methanol by-products. This self-Cannizzaro reaction consumes formaldehyde, so it is necessary to use a controlled amount of formaldehyde, acetaldehyde, and alkali media at optimum reaction conditions to drive the reaction in the desired direction [25]. During the penta synthesis reaction, many other side reactions can occur, which resultantly reduce the selectivity for penta. As shown in Scheme 3, there could be four different types of side reactions occurring, such as (1) polymerization reaction of formaldehyde to form trioxane or other long chain formaldehydes, (2) the self-Cannizzaro reaction of formaldehyde, (3) acetaldehyde self-condensation reactions, and (4) penta derivatization reactions. The formation of sodium formate always occurs in the alkaline liquid solution, as this is a product of the Cannizzaro reaction when pentaerythrose converts to penta [16]. In penta-derivatization side reactions (4), penta reacts with formaldehyde in the reaction mixture to form different derivatives, [26–31] such as linear hemiacetals of penta, cyclic monoformals of penta (CPF), and dipentaerythritol (dipenta), as shown in Scheme 3. Therefore, it is highly desirable to isolate the produced penta from the reaction mixture to preserve its selectivity. From a reaction engineering perspective, it is possible that residence time or space velocity in the reactor could be used to control the by-product formation from penta-derivatization.

Producing penta with high-yield and high-quality industrially through the conventional alkaline synthesis route is challenging. According to Tribula et al. yield losses mainly occur during the penta separation steps – such as flashing, crystallization, filtration, and decolourization – that are needed to obtain pure penta [32]. The first industrial penta synthesis processes were started in the early 1890 s, and since then significant improvements have been made to enhance both separation steps and the resulting yield. However, the knowledge that exists in the literature is rather fragmentary, so this review aims to collect, analyse, and evaluate the available findings. A recent review article has covered the multitude of applications of penta for the synthesis of many organic and medicinal products [1].

However, there is a noticeable lack of literature reviewing advances in the development of efficient processes for producing penta. This review is according to our knowledge, the first summary of the state-of-the-art knowledge of penta synthesis through homogeneous catalysis processes. The main contributions of this work are as follows: (1) A comprehensive review of research progress in pentaerythritol synthesis processes, highlighting the key factors influencing penta selectivity along with other side products. (2) An analysis of separation strategies to enhance penta yield by reducing penta contact with the reaction mixture. (3) An overview of challenges and future research opportunities in penta synthesis, emphasizing critical parameters for optimizing the reaction and advancing catalyst development.

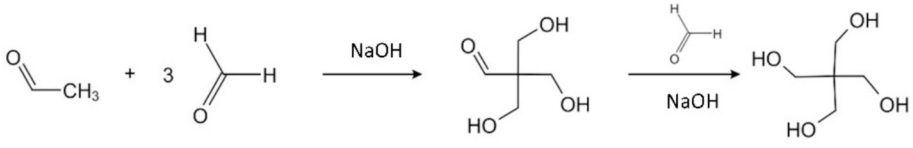
Penta synthesis process

There are several patents that describe good reaction conditions and different separation steps to obtain a high yield of penta. Three independent variables such as the initial molar ratio of formaldehyde/acetaldehyde, NaOH/acetaldehyde, and the initial concentration of aldehydes in the reaction mixture are the central key parameters that affect the process conversion and yield [33].

Aldehydes ratio effect on penta synthesis reaction

One study recommends using formaldehyde in excess, with a formaldehyde-to-acetaldehyde molar ratio of 5:1 to achieve a favourable reaction extent. In the same study, it was also reported to use 10 % excess of the theoretical amount of required NaOH to compensate for its consumption in forming the alkali formate through the Cannizzaro reaction. This excess of formaldehyde complicates its recovery and the separation of penta crystals from the synthesis solution. Moreover, to stop the reaction it is required to neutralize the excess NaOH with an acid such as formic acid or sulphuric acid [23]. The optimum amount of acetaldehyde in the reactor feed is also an important parameter to control the product distribution. Patent WO2020/067963 [34] shows that increasing the acetaldehyde amount or reducing the formaldehyde to acetaldehyde ratio in the reaction system boosts dipenta yield. This is due to that less formaldehyde in the system forms more acrolein which is very reactive and takes part in the synthesis of dipenta. Along with this, the formose reaction becomes a side reaction under such conditions, producing higher sugars which thus consume formaldehyde at the expense of the desired reaction to produce mono-pentaerythritol [34]. These higher sugars can later break down to give glycolaldehyde. The measure of glycoladehyde gives an indirect measure of the formation of higher sugars in the system and it also causes the product solution to turn yellow and brown [34]. To optimize the reaction, continuous dosing of acetaldehyde, calcium hydroxide, and half of the formaldehyde over 40 to 60 min was recommended by Månsson et al. and residual formose inhibitors are removed via ion exchange. It was also suggested by the same inventors to pause the continuous feeding of formaldehyde for 5 to 20 min during the reaction, as this improved the synthesis of dipenta, increasing its yield to 8 % [34]. To avoid the usage of a large amount of formaldehyde during the synthesis process, a continuous process with a series of reactors was introduced in a patent in 1960 to minimize the formation of by-products [35]. For this purpose, acetaldehyde and NaOH were fractionally introduced during the reaction in multi-stage reactors in series. In the reactor, formaldehyde was added from the bottom and acetaldehyde and NaOH was continuously added from upward nozzles at a molar ratio formaldehyde:acetaldehyde:NaOH = x:1:y (where x = 4.5–8 and y = 1–1.3) at 40–60 °C. It was claimed that, under this operating regime, it was possible to achieve an 87 % yield of penta based on acetaldehyde and 77 % yield based on formaldehyde with a good quality as measured by the color quality grade [35].

In comparison to the cascade/series arrangement of reactors, in a later work, a continuous flow of acetaldehyde and NaOH from separate buffer tanks was introduced into a single reactor that initially contained the full formaldehyde feed. With the gradual feed of NaOH, the pH of the reaction mixture was controlled [25]. The first reaction step was carried out at a high pH of 10–11 to obtain the pentaerythrose intermediate and later the pH was reduced to perform the Cannizzaro reaction. Of course, the formation of sodium formate was also observed in the second step. The raw pentaerythritol which contained 80–90 % mono penta and 10–14 % dipenta, was then subjected to high temperature acid hydrolysis and decolourization. It was further reported by the author that the Cannizzaro reaction is relatively slow at low temperatures of 20–30 °C, whilst the condensation reactions are faster in this same low



Scheme 1. General reaction for the synthesis of Pentaerythritol.

temperature range [25]. It was suggested to raise the temperature of the reaction mixture once all the acetaldehyde was consumed to favor the Cannizzaro reaction. It was concluded in the patent that the different possible reactions strongly depends on pH, temperature, concentrations, the amount and sequence of reactant addition, and time, and thus, optimized conditions are needed to achieve a high yield of penta [25].

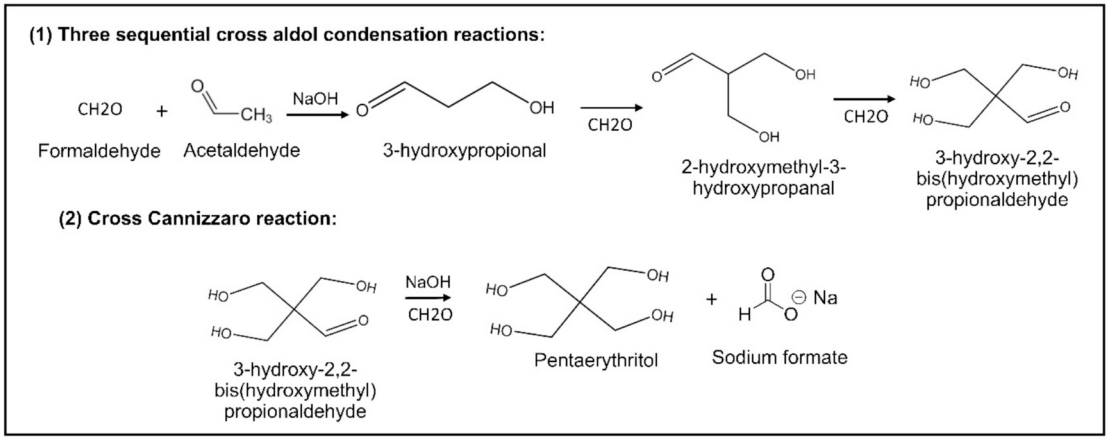
Amount of water and dilution effect on synthesis reaction

Formaldehyde exists as a gas under ambient conditions, making it difficult to handle. It is commonly used in an aqueous solution form known as formalin, which typically contains 37–40 % formaldehyde in water. In the penta synthesis process, the amount of water in the reaction mixture is also a key parameter to ponder, and usually it is considered as the formaldehyde feed concentration in water. It has been reported that a higher concentration of formaldehyde in the reaction mixture facilitates the formation of dipenta and tripentaerythritol, while on the other hand more water in the system slows down the reaction and increases the eventual evaporation load during the product separation [16]. The optimum value for the formaldehyde concentration was suggested to be in the range of 12–20 % in aqueous solution [16]. To increase the flexibility of the penta synthesis process, it was recommended in a Russian patent RU2445303C1 [36] to use paraformaldehyde granules instead of an aqueous solution of formaldehyde as the life of the formaline solution is short and it must be stored at 60 °C according to the inventors [36] to prevent polymerization which complicates the process. Paraformaldehyde exists as a solid form of polymeric formaldehyde. However, an extra dissolution step of paraformaldehyde in water at 40 °C is needed before adding the caustic soda and acetaldehyde to initiate the condensation reaction [36].

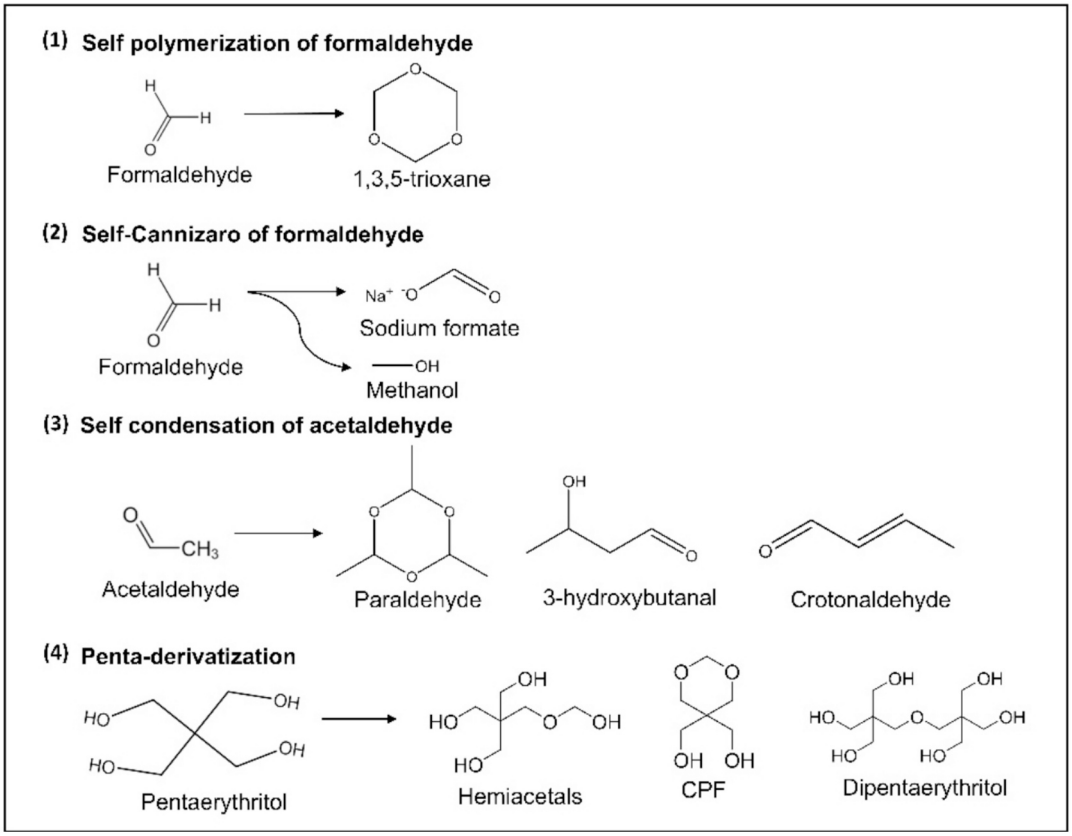
Influence of the catalyst on penta yield and formates separation

It was also reported in the same patent that the use of a calcium based alkaline solution in the system is favourable to produce dipenta and that the byproduct calcium formates have a higher market value compared to sodium-based formates [34]. In 2024, an invention outlined a method to synthesize penta by recycling the calcium hydroxide solid waste as calcium carbide slag, used as a catalyst, which is a byproduct of the PVC manufacturing process via the acetylene method [37]. However, the overall process becomes more complex when calcium carbide slag is used as, (1) an anti-saccharification auxiliary agent, alkali metal molbydate in formaldehyde, is added to avoid formose formation; (2) a finishing agent, which is a 1:1 M mixture of KCN and NaCN, is used to ensure the uniform crystallization of penta; (3) an emulsified silicon oil as a precipitant is used after the completion of the condensation reaction; and (4) the process results in calcium formate solids with strong adhesive properties, which lead to equipment blockage issues [37]. Interestingly, in another study the sodium formates produced as a byproduct were purified through an additional distillation step and the crystals obtained were redissolved and reacted in water with lithium chloride to obtain lithium formate and sodium chloride. It was proposed in this invention, to convert the waste sodium formate into more valuable lithium formate to reduce the amount of the secondary pollutant [38]. A method was also developed to address the separation issues of sodium formate by using oxalic acid to adjust the pH of the product filtrate, resulting in the formation of sodium oxalate instead of sodium formates. The oxalates can be easily separated out at room temperature and a sodium yield of almost 98 % could be obtained [39]. Sodium formates have been separated out at higher temperatures which leads to the formation of other byproducts and makes the process more energy intensive and less efficient [40–42]. Several separation techniques for purifying sodium formate were patented in the late 1900 s including the use of acrylic/porous resins [42,43], methanol esterification [44,45], fatty acid esterification [46], and electrodialysis [47]. However, these processes have disadvantages such as poor pentaerythritol yield, high costs and increased complexity in the penta synthesis process. Later in the early 2000 s, various patents reported the use of liquid–liquid extraction for sodium formate separation with different extracting agents such as isobutanol [48,49], and tetrahydrofuran [50] but these methods also had large challenges, due to poor penta yield, high costs, and process safety issues. More recently in 2022, a solid-phase extraction-elution crystallization method, along with a purification device was developed to separate sodium formate from the penta mixture [51,52]. This method improves the purity of sodium formate and the recovery of pentaerythritol but still faces challenges with solvent separation and recovery, as the extraction temperature remains as high as 120 °C. In order to address the shortcomings of the process reported in patent CN112745214A [51] in 2022, another patent CN115710176A [53] in 2023 described a modified method in which water and methanol was used as the extraction solvent at relatively low temperature to improve the solvent recovery. Also, a multi-stage sedimentation method has been reported to separate out the sodium formate from the pentaerythritol mother liquor, achieving a 98-grade product purity in 2023 [54].

A production method with potassium hydroxide as a catalyst was also reported in a study where potassium formate was obtained as a byproduct with 96 % mass content with the aim of reaching the requirement for use as a drilling fluid [55]. Additionally, as an alternative to the NaOH liquid solution catalyst, a solid anion exchange resin (anionite) was used to manufacture penta, marking the first reported use of a type of heterogeneous catalyst alternative [32]. During the reaction forming penta, formic acid is a by-product adsorbed onto the catalyst,



Scheme 2. A sequential condensation of three molecules of formaldehyde on the α-carbon of acetaldehyde (1) and the Cannizzaro reaction of the final condensation compound (2) to form pentaerythritol and formate [16,17].



Scheme 3. Side reactions that can occur during penta synthesis.

and unfortunately effectively consuming it. Consequently, a sodium hydroxide solution must periodically regenerate the catalyst, producing sodium formate. An advantage with this process is that it generates a stream of sodium formate with excess sodium hydroxide separate from a stream of penta with excess reactants and other by-products [32]. The performance metrics of different catalytic systems for penta synthesis have been summarized in Table 1. Most recently in 2025, density functional theory calculations were performed to provide mechanistic insights into the role of alkalinity on the formaldehyde used in the synthesis of pentaerythritol. It was concluded that industrial alkaline formaldehyde in the form of a sodium solvation cage with a *hexa*-co-ordinated state, effectively regulates the solvent alkalinity favoring the aldol and Cannizzaro reactions as shown in Fig. 1. This first ever article presenting a detailed molecular path for the penta synthesis reaction with the quantification of the activation energies of different steps [56]. It was also discussed in the article that feeding weak and strong bases in segments can control the aldol and Cannizzaro reaction respectively and improve the yield by 7–13 % [56].

Temperature dependence of yields

Temperature adjustment during the penta formation reaction can be crucial for improving both penta selectivity and yield. This is because penta formation is not a single step reaction but instead involves a multi-step condensation and a Cannizzaro reaction, all of which can have different temperature dependence. The yield of penta is strongly sensitive to temperature, at higher temperature a maximum of 77 % overall polyols yield is obtained containing 83 % monopentaerythritol at 84 °C, as shown in Fig. 2 [16]. A small variation in the temperature can lead to the formation of many byproducts and the yield of penta can as a result be reduced. It has been reported in the same study that the use of a lower initial temperature of 25 °C followed by an increase to 45 °C after some time, improves the selectivity and yield.

Pyro-condensation with the concatenate recrystallization is a

Table 1
Performance metrics of different catalysts in Penta synthesis.

Catalysts	Monopenta selectivity (%)	Advantages	Disadvantages	References
$Ca(OH)_2$	Unspecified	High market value of calcium formate	Form more dipenta and calcium formate	[34]
Calcium carbide slag	98.2	Solid waste of PVC manufacturing plant used as catalyst	Multiple auxiliary agents used including anti-saccharification, flocculationg, and precipitant agents. Equipment blockage issues.	[37]
NaOH	80–90	Mature industrial catalyst that has undergone extensive optimization	Sodium formate typically difficult to separate so several techniques has been used to get pure sodium formate stream and to convert it into a valueable product	[38–54]
KOH	98.5	No equipment clogging, and 96 % pure potassium formate obtained, meeting requirements for drilling fluids	Ash formation from KOH impurity	[55]
Solid anionite resin	Producing both off-grade penta and pure penta streams without specifying purity levels.	A separate stream of sodium formate and unreacted NaOH from penta simplifies the process	Resin regeneration is needed due to the adsorption of by-products on its surface	[32]

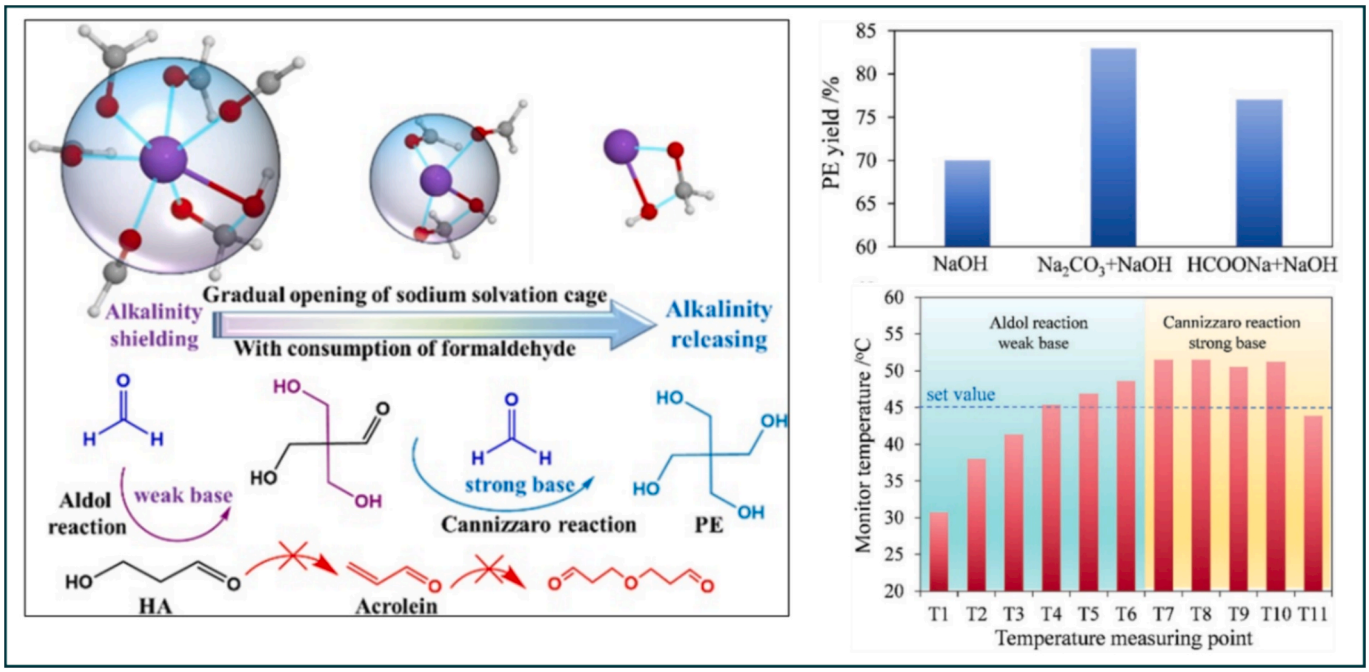


Fig. 1. Alkalinity effect on aldol and Cannizzaro reaction to produce pentaerythritol. Reprinted from Chinese Journal of Chemical Engineering, Vol. number 79, Author(s), Zhengguang Wang, Xin Qu, Xingke Yuan, Zhanpeng Gao, Niu Hu, Jiansheng Wei, Wenpeng Li, Zhirong Yang, Jingtao Wang, title of article: Continuous-flow synthesis of pentaerythritol: Alkalinity release of sodium solvation cage to control aldol and Cannizzaro reactions, Pages No. 23–29, Copyright (Year 2025), with permission from Elsevier.

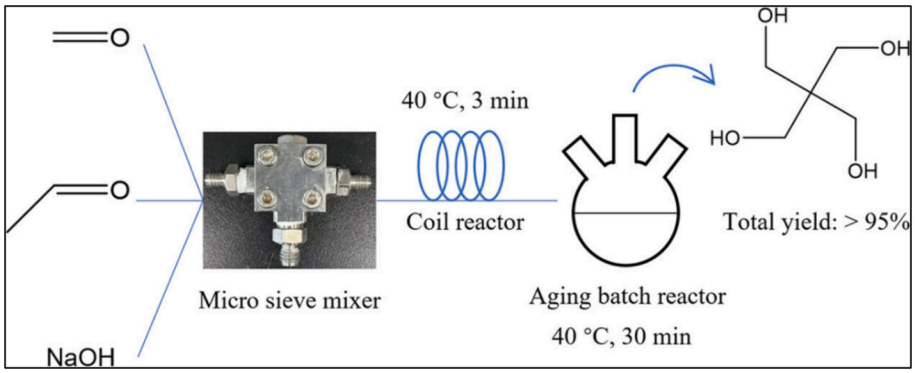


Fig. 2. Microreactor system with controlled temperature to produce pentaerythritol. Reprinted with permission from reference [57]. Copyright 2025 American Chemical Society.

concept that was introduced in patent CN1736969A where the high temperature condensation reaction and recycling of the mother liquor stream in each recrystallization step is introduced [58]. This process helps to reduce the raw material consumption, increase the economic efficiency, and minimize the waste discharge but the mono-pentaerythritol yield was compromised as dipenta and formates were also produced [58]. Interestingly, in another study on the condensation reaction, formaldehyde was first mixed with an alkaline solution, followed by the controlled addition of acetaldehyde at 2–10 min later to efficiently manage the heat exchange. The reaction proceeded for 30 to 100 min, reaching temperatures of 45 to 70 °C under 0.2 MPa pressure. After a two-step purification process 98.3 % mono-pentaerythritol was obtained with an overall yield of 94.2 % [59]. In 2024, a patent claims to improve the monopenta synthesis with 99.0–99.6 % (yielding 90–93 % organic matter based on GC analysis) by lowering the formaldehyde to acetaldehyde ratio to 4–5:1. The process involves mixing the reactants in an ice bath followed by adding the NaOH solution dropwise at 10 °C or below, and then slowly heating to 40 °C after 0.5 h [60]. The summary of

Table 2
Penta synthesis at different temperatures and its impact on the yield of penta.

Temperature	Overall Yield of polyols (penta and dipenta) (%)	Monopentaerythritol (%)	Remarks	Reference
84	77	83	Gradual temperature increase improves the yield	[16]
45–70	94.2	98.3	Controlled addition of acetaldehyde	[59]
10–45	90–93	99.0–99.6	Slow heating	[60]
40	>95	88	Controlled temperature	[57]

the different temperature effect on penta yield is reported in Table 2.

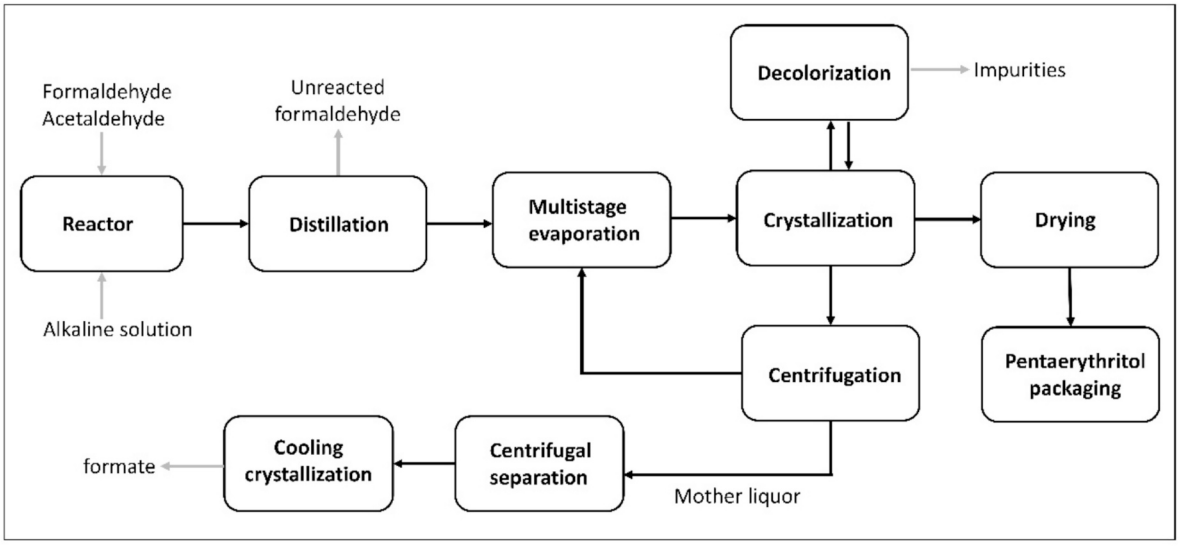
Very recently in 2025, a continuous micro-reaction system was constructed for intensifying and regulating the homogeneous aldol reaction combined with a batch reactor for conducting the Cannizzaro reaction [57]. Due to the excellent mixing performance of the micro-reactor and accurate temperature control, the penta reaction time was reported to be reduced to 1/8th of conventional processes and 88 % yield of penta was achieved and the total yield containing by-products was > 95 %. This study highlighted the rapidity of the reaction steps (aldol reaction completed in 3 min), and the resulting importance of control of temperature and reactant mixing, as shown in Fig. 2. The microreactor system was claimed to be suitable for future studies of reaction kinetics [57].

Separation techniques and yield Improvement

In a typical industrial synthesis process of penta, aldehydes undergo condensation and the Cannizzaro reaction in the presence of an alkaline solution to form penta, as described in the introduction section of this review. This penta in the reaction mixture of unreacted aldehydes, water, formates and other by-products passes through a distillation column where unreacted formaldehyde is separated out as shown in Scheme 4, which is based on references [16,25,61,62]. After multistage evaporation, several crystallizations, centrifugation, drying and decolorization steps, penta with the desired purity and yield is separated out along with formates (Scheme 4).

In most industrial processes, after the appropriate reactor space time and then neutralizing the excess of NaOH, the reaction mixture is cooled to 10 °C to crystallize the first crop of penta [16,61]. The crystals are then separated out by centrifugation. Different steps of crystallization and centrifugation units are used as shown in Scheme 4 to obtain product of a desired purity level [47,63]. For example, the yield obtained from the first crop was reported to be typically 75 % of the total product [16]. The obtained liquid can be further concentrated to improve the yield of penta crystals. The residual mother liquor mainly consists of sodium formate salt and a small amount of penta and other polyhydroxy compounds. Polyhydroxy compounds like penta and dipenta can be separated out from each other based on their solubility in water as explained in the invention GB772574A [64]. In 2006, patents were published regarding the invention of evaporation crystallization [65] and cascade recrystallization [61] processes to recover penta from reaction mixture. In cascade crystallization compared to the process shown in Scheme 4, to improve penta yield at low cost, the reaction is carried out at lower temperatures, thereby eliminating the need for subsequent cooling using a refrigerant [61]. The proposed separation technology offers the advantage of recycling the mother liquor obtained after each crystallization step which in turn improves the atom economy and yield of penta to 95–99 %. However, the weakness in this process is the production of many byproducts and uncontrolled side reactions [61]. Many other Chinese patents have discussed the same low–high temperature method for preparing mono-penta but also face the same issues as discussed above [66,67]. In a US patent in 2009, a purification step with ion exchangers was applied to remove the possible byproducts and impurities and the purity of mono-penta was reportedly improved to 99.9 wt%. It was further investigated in the patent the relation between the formaldehyde: acetaldehyde ratio and the crystallization temperature for obtaining a high-grade yield. It was found that at a 5:1 ratio, a crystallization temperature of 55–90 °C was best for high yield, whereas by further increasing the reactant molar ratio to 9:1, the optimal crystallization temperature reduced to 45–60 °C [68]. In another patent, the wastewater stream containing unreacted acetaldehyde and formaldehyde was processed to recycle back the aldehydes. For this purpose, the process water containing formaldehyde, acetaldehyde, formic acid and acetic acid was evaporated at 90–100 °C, and the pH of the obtained recycle stream was then adjusted and pumped back to a recovery tank. The proposed method was considered eco-friendly and also increased the yield of formaldehyde and acetaldehyde [69]. A three-stage crystallization process was introduced to enhance the quality of the final penta crystals, to achieve better dispersibility, larger crystal size, and full particles which eases filtration [62]. In stage (1) an alcohol solution in the crystallization tank was added and then the contents were cooled at 4–6 °C/h to reduce the temperature to 95 °C, in stage (2) penta seed crystals were added amounting to 1 wt% while cooling at a rate of 1–3 °C/h to 90 °C, in stage (3) crystal growth occurred at a constant temperature of 85–95 °C during 1–2 h. In the final stage (4) the solution was then moderately cooled to 70 °C at a rate of 5 °C/h, after which the crystals were then distilled, centrifuged, washed and dried for packing [62].

The formation of penta derivatives is a key factor influencing the purity of the penta obtained in the synthesis process. Pentaerythritol monoformals usually form due to the condensation of monopentaerythritol with formaldehyde. It has been previously reported that hydrolyzing these formals in the presence of a mineral acid at boiling conditions can improve the yield of pentaerythritol. However, despite its purported strengths, a poor yield was obtained with this method due to the degradation of the mineral acid and pentaerythritol as well [70].



Scheme 4. A general block flow diagram for synthesis process of pentaerythritol.

Later improved pentaerythritol yield was achieved with a suitable process by simply heating the aqueous solution of formals at 150–300 °C in the presence of a cracking catalyst such as silica with metal oxides. In this process, an enhanced penta yield was obtained, however, a practical limitation was the need for a large amount of water for hydrolysis [71]. Efforts were also made by Korean investigators to purify the penta from the mother liquor by sequentially repeating the crystallization processes and a reported yield of 99.5–99.9 % was achieved [72,73]. A patent CN202222545758 reported the invention of a high-purity purification process including several dissolving towers, an aldehyde take off device, filtration equipment, a decolorization bed, a recrystallization tower, and many other auxiliaries to separate out the impurities step by step, so the purity was improved for mono penta [74]. Compared to the above mentioned separation process equipment, another more compact separation device was invented recently in 2023 to isolate penta from the reaction mixture. This device offers a simpler separation process in a single vessel; however, no information was given regarding the capacity of this unit or its scalability. The reported device consists of a churn connected to an inlet pipe, a bottom heating mechanism for evaporation, and a stirring system. It incorporates a method for stratifying the mother liquor, along with a specialized liquid extraction device enabling the separation of penta in liquid form into layers from the mother liquor [75].

A method for preparing 95 grade penta was introduced in patent CN104230660A, where the basic steps included condensation and preheating, dealdehyding and triple effect evaporation. However, some additional steps were introduced to achieve a high purity of penta such as heating the mixed liquid obtained from a triple-effect evaporator. Centrifugation of the cooled mixed liquid at higher temperature i.e., 80–90 °C and further drying to finally obtain the 95 grade mono-penta [76]. However, this method caused the formation of other byproducts and a high acetal content. In addition, the automation degree of this method was low which consequently increased the operating costs for the penta synthesis. To address these issues, another patent introduced a 99-grade penta production method in which the shortcomings of the prior method were resolved to enable a continuous one-step production of penta with lower acetal formation [77]. In another study, the inventors claimed to achieve 99.3 % purity of penta using the conventional condensation reaction procedure, followed by a separation step involving the evaporation of the reaction mixture to obtain 50–70 % solids. The solids were then cooled and penta was isolated using a band filter. The isolated penta was dissolved in a 35–55 % aqueous solution and purified by crystallization from the solution at 40–90 °C. The crystals were separated from the mother liquor, which was subsequently recycled [78]. In a US patent, the ozone-air mixture along with the acid treatment was used to crack the formals and to remove the colour from the crude penta [63]. Table 3 shows the summary of the different separation techniques that has been discussed above and reported in literature.

Conclusions and perspectives

Pentaerythritol is an essential platform chemical that is used in manufacturing industries. The industrial synthesis process of penta includes condensation and Cannizzaro reactions of aldehydes in the presence of an alkaline solution acting as a homogeneous catalyst. There are a number of patents that describe processes designed to achieve high purity and yield of penta, but these often come at the cost of increased expense and energy consumption. A high purity and yield of penta demands a complex separation process, as several byproducts form during penta synthesis. For example, sodium formate, and polymers of penta are the main byproducts from the synthesis process. Therefore, in the inventions discussed in this review, the inventors developed different techniques to purify and separate byproducts along with penta, aiming to minimize waste during the synthesis and enhance the atom economy of the overall manufacturing process. Several inventions discuss the influence of important parameters for the synthesis, for example, the control of temperature during reaction, molar ratios of aldehydes and catalyst, amount of water, and reaction time to improve the yield of penta. Also, there are studies investigating the development of alternative catalysts or combinations of catalysts for the reaction process. Examples of catalysts studied to produce penta include calcium slag waste and ion exchange resins. One catalyst may be more efficient than another in terms of penta selectivity, but all of the studies discussed above consistently faced the issue of catalyst consumption due to its reaction with formaldehyde to form formate.

There are different research gaps that can be pointed out from the above literature review, requiring further investigation.

(1) A more systematic analysis of variations or alternatives of penta separation processes comparing the costs in terms of energy and capital costs of equipment with the overall improved efficiency of the process in terms of product yield and purity.

(2) Research is lacking that investigates means of integrating the reaction and separation processes to achieve improved energy and material efficiency.

(3) Most reported studies on penta synthesis are primarily

Table 3
Summary of different separation technologies used to improve penta yield and purity.

Separation Process	Conditions	Purity	Remarks	Reference
Evaporation crystallization	100 °C, 50–500 mmHg	85–98 %	Industrial grade penta	[65]
Cold crystallization	160–190 °C, 15–60 min	97 %	BPE removal	[65]
Cascade recrystallization	Multi-step separation	95–99 %	Uncontrolled side reaction	[61]
Ion exchange	5:1, 55–90 °C	99.9 %	Aldehydes amount effect on crystallization temperature	[68]
Waste stream recycling	Mother liquor stream heated at 90–100 °C and recycled	Aldehydes yield improved	emissions reduced	[69]
Multi-stage crystallization	Repeated crystallization	99.5–99.9 %	Mother liquor purification	[62,72,73]
Purification device	Multiple separation steps	98 %	Process with 10 different units (i.e., dissolving towers, aldehyde removal device, filtration, decolorization bed, recrystallization tower, and other auxiliaries)	[74]
Formals hydrolyzation	Boiling acid with formals	Formals removal	Degradation of penta and mineral acid	[70]
Formals heating	150–300 °C, cracking catalyst	Formals removal	Large water amount is required	[71]
Separation device unit	Compact device with 17 different parts	Efficiency improved	Scalability concern	[75]
Tripple effect evaporator	80–90 °C	95-grade	By-products formation, high operating cost	[76]
Automatic production line	8 separation units	99-grade	Less labor	[77]
Conventional synthesis and separation	Several separation steps	99.3 %	Recycled mother liquor	[78]
Acid-Ozone Treatment	2.2 pH, 90–105 °C,	0.5 % formals	Formals cracking and decolouration	[63]

experimental, whereas kinetic modeling based on experimental data is rare — only two such studies have been found [22,79]. In the study by Belkin et. al. [79], a mathematical model was developed that incorporates reaction rate equations for penta and its derivatives (based on their reaction schemes), formulas for calculating activity coefficients, activation energies, degrees of ionization, and equilibrium concentrations of intermediate species. Moreover, the authors concluded that this model can be applied to evaluate the efficiency of penta synthesis in various types of reactors [79]. An older study by Peters in 1958 investigated the kinetics of reactions involved in penta synthesis [22]. The study revealed that aldol condensation leading to pentaerythrose formation occur very rapidly, even at low concentrations of pentaerythrose, while the rate-limiting step is the Cannizzaro reaction [22]. Activation energies and rate constant equations for both aldol and Cannizzaro reactions were reported, using NaOH as the base catalyst. Peters also noted that the side reactions during the rapid aldol condensation can redue the penta yield [22]. More recently in 2025, Wang et. al. employed density functional theory (DFT) calculations to show that the aldol reaction has a lower activation energy than the Cannizzaro reaction, emphasizing the importance of temperature control in achieving reaction selectivity [56]. Their study also found that segmented feeding of weak and strong alkaline solutions favors the aldol and Cannizzaro reactions, respectively [56]. Beyond reaction kinetics, crystallization kinetics of penta in a suspension crystallizer were studied in 1996 [80]. Kinetic models for crystal growth, attrition, and secondary nucleation were developed and validated using optical measurements [80]. Further development of kinetic models, could significantly improve optimization of the reaction and its integration with separation steps. For example, it has been experimentally observed in some studies that variation of reaction conditions such as temperature or reactant concentrations, during the synthesis, can improve penta yield. Development of a comprehensive kinetic model would therefore be a valuable tool for effectively optimizing penta synthesis under varying reaction conditions.

(4) It would also be beneficial to further develop heterogeneous catalyst systems to replace the homogeneous catalysis route of penta synthesis, and eliminate the need for the liquid alkaline solution. A solid catalyst should ideally be easily regenerated. More importantly, its transport through the process could be avoided, and separation steps for its recovery simplified which is a major challenge with the conventional penta synthesis. The use of a solid alkaline resin has been reported to offer some of these advantages by keeping the penta and formates streams separate, thereby simplifying the separation process [32]. However, challenges remain, including catalyst regeneration and deactivation caused by formic acid by-product deposition on the resin surface. The greatest challenge today lies in achieving high penta selectivity and catalyst stability, as there is a significant gap in the existing literature on penta synthesis processes.

(5) An interesting alternative is to explore the use of different reactants instead of aldehydes with different reaction mechanisms that could avoid the byproduct formation, such as formates and penta-derivatives. For example, sugar-based compounds could have the potential to utilize the chemistry of sugars, using enzymatic or thermal catalytic systems to rearrange the carbon chain and hydroxyl groups of sugars to other polyols like penta. This is, however, a challenging approach, although innovative, since there is no literature to our knowledge in this area.

(6) Dipenta is in high demand and is currently produced commercially as a by-product of penta. A potential way forward is to develop processes that minimize by-product formation during penta production, followed by selective derivatization of penta to obtain dipenta. Recently, an efficient process has been patented for penta dimerization to produce dipenta [81].

CRediT authorship contribution statement

Aqsa Noreen: Writing – original draft, Methodology, Investigation, Conceptualization. **Derek Creaser:** Writing – review & editing, Supervision, Conceptualization. **Oleg Pajalic:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Louise Olsson:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This project was conducted at the Chemical Engineering division, the Competence Centre for Catalysis (KCK) and the Centre for Process Chemical Engineering (CPE) at Chalmers University of Technology, and was performed in collaboration with Perstorp AB. We gratefully acknowledge the funding from Swedish Energy Agency (P50869-1) and NextGenerationEU (The Recovery and Resilience Facility, RRF).”

Data availability

Data will be made available on request.

References

[1] Z. Khademi, K. Nikoofar, F. Shahriyari, Pentaerythritol: a Versatile Substrate in Organic Transformations, Centralization on the Reaction Medium, Curr Org Synth. 16 (1) (2019) 38–69, https://doi.org/10.2174/1570179415666181115102643.
[2] W.X. Chen, X.D. Fan, Y. Huang, Y.Y. Liu, L. Sun, Synthesis and characterization of a pentaerythritol-based amphiphilic star block copolymer and its application in controlled drug release, React. Funct. Polym. 69 (2) (2009) 97–104, https://doi.org/10.1016/j.reactfunctpolym.2008.11.006.
[3] H. Ji, B. Wang, X. Zhang, T. Tan, Synthesis of levulinic acid-based polyol ester and its influence on tribological behavior as a potential lubricant, RSC Adv. 5 (122) (2015) 100443–100451, https://doi.org/10.1039/C5RA14366G.
[4] D. G. van der Poll, H. M. Kieler-Ferguson, W. C. Floyd, S. J. Guillaudeu, K. Jerger, F. C. Szoka, J. M. Fréchet Design, synthesis, and biological evaluation of a robust, biodegradable dendrimer, (in eng), *Bioconjug Chem,* Bioconjug Chem 21 (4) (2010) 764-773. DOI: 10.1021/bc900553n.
[5] P.J. Garegg, R. Johansson, C. Ortega, B. Samuelsson, Novel reagent system for converting a hydroxy-group into an iodogroup in carbohydrates with inversion of configuration, J. Chem. Soc. Perkin Trans. 1 (1982) 681–683, https://doi.org/10.1039/P19820000681.
[6] N. Jahan, N. Paul, C. J. Petropolis, D. G. Marangoni, T. B. Grindley, Synthesis of Surfactants Based on Pentaerythritol. I. Cationic and Zwitterionic Gemini Surfactants, The Journal of Organic Chemistry, 74 (20) (2009) 7762-7773. DOI: 10.1021/jo9018107.
[7] M. Saucier, C. Sauriol, R.L. Salvador, AMÉLIORATION DE LA SYNTHÈSE DES DI- ET TRI-BROMHYDRINES DU PENTAÉRYTHRITOL, Can. J. Chem. 44 (13) (1966) 1599–1601, https://doi.org/10.1139/v66-241.
[8] H. de la Rosa-Ramírez, F. Dominici, J.N. Ferri, F. Luzi, D. Puglia, L. Torre, J. López-Martínez, M.D. Samper, Pentaerythritol and Glycerol Esters Derived from Gum Rosin as Bio-based Additives for the Improvement of Processability and thermal Stability of Polylactic Acid, J. Polym. Environ. 31 (12) (2023) 5446–5461, https://doi.org/10.1007/s10924-023-02949-0.
[9] B. Tang, W. Feng, J. Guo, J. Sun, S. Zhang, X. Gu, H. Li, W. Yang, Hydrophobic modification of pentaerythritol and its application in fire-retardant coatings for steel structures, Prog. Org. Coat. 138 (2020) 105391, https://doi.org/10.1016/j.porgcoat.2019.105391.
[10] R.K. Singh, A. Kukrety, A.K. Singh, Study of Novel Ecofriendly Multifunctional Lube Additives based on Pentaerythritol Phenolic Ester, ACS Sustain. Chem. Eng. 2 (8) (2014) 1959–1967, https://doi.org/10.1021/sc500389f.
[11] S. S. Saei Dehkordi, J. Albadi, A. A. Jafari, H. A. Samimi, Boric Acid/Pentaerythritol as a Green and Reusable Catalytic System for the Synthesis of Mono- and Bis-Pyrano[2,3-d]Pyrimidinone Derivatives in Water, Polycyclic Aromatic Compounds, 43 (5) (2022) 1-12. DOI: 10.1080/10406638.2022.2118330.
[12] R. Niu, Z. Zheng, X. Lv, B. He, S. Chen, J. Zhang, Y. Ji, Y. Liu, L. Zheng, Long-Chain Branched Bio-based Poly(butylene dodecanedioate) Copolyester using Pentaerythritol as Branching Agent: Synthesis, Thermo-Mechanical, and Rheological Properties, Polymers 15 (15) (2023) 3168, https://doi.org/10.3390/polym15153168.

[13] H.A. Mahmud, N. Salih, J. Salimon, Oleic acid based polyesters of trimethylolpropane and pentaerythritol for biolubricant application, Malaysian Journal of Analytical Sciences 19 (1) (2015) 97–105.
[14] Z.A. Maurad, S.K. Yeong, Z. Idris, S.A. Ishak, Combined Esterification and Short-Path Distillation for High-Purity Pentaerythritol Ester from Palm Kernel for Biolubricants, J. Am. Oil Chem. Soc. 95 (11) (2018) 1421–1429, https://doi.org/10.1002/aocs.12149.
[15] A.S. Amarasekara, U. Ha, N.C. Okorie, Renewable polymers: Synthesis and characterization of poly(levulinic acid–pentaerythritol), J. Polym. Sci. A Polym. Chem. 56 (9) (2018) 955–958, https://doi.org/10.1002/pola.28980.
[16] M.S. Peters, J.A. Quinn, Pentaerythritol Production yields, Industrial & Engineering Chemistry 47 (9) (1955) 1710–1713, https://doi.org/10.1021/ie50549a016.
[17] S. Jiang, Z. Li, L. Zhao, M. Sun, X. Zhang, D. Yang, G. Xu, Synthesis of 1,3-Propanediol by Cross Aldol Reaction and Hydrogenation of Formaldehyde with Acetaldehyde, ACS Sustain. Chem. Eng. 10 (7) (2022) 2355–2367, https://doi.org/10.1021/acssuschemeng.1c06393.
[18] E. Edward A., Acetaldehyde-Formaldehyde Condensation Product, US2325589A, 1941.
[19] K.Y. Fukuda Takeshi, N. Takeshi, O. Shinji, Production of dipentaerythritol, JP3791960B2 (1996).
[20] M. Landart, M. Lemaire, E. Métay, Synthesis of Dipentaerythritol from Pentaerythritol under Acidic Conditions, Org. Process Res. Dev. 24 (11) (2020) 2591–2603, https://doi.org/10.1021/acs.oprd.0c00269.
[21] L. Li, Y. Kamiya, T. Okuhara, Catalytic dehydration of pentaerythritol to dipentaerythritol over heteropoly compounds, Appl. Catal. A 253 (1) (2003) 29–32, https://doi.org/10.1016/S0926-860X(03)00495-2.
[22] M.S. Peters, C.R. Cupit, Kinetics of pentaerythritol-production reactions, Chem. Eng. Sci. 10 (1) (1959) 57–67, https://doi.org/10.1016/0009-2509(59)80025-7.
[23] L. Eek, Process for the formation of Pentaerythritol, US5741956A (1997).
[24] L. Koudelka, Reactions of acetaldehyde in the preparation of pentaerythritol, Chem. Zvesti. 37 (3) (1983) 374–383.
[25] L. Eek, Process for the Preparation of Pentaerythritol, US005741956A (1998).
[26] S.F. Marrian, The Chemical Reactions of Pentaerythritol and its Derivatives,", Chem. Rev. 43 (1) (1948) 149–202, https://doi.org/10.1021/cr60134a004.
[27] G.R. Owens, Process for preparation of pentaerythritol, US40150741A (1945).
[28] L.W. Trevoy, M.E. Myers, Pentaerythritols derivatives: Mechanism of formation of dipentaerythritol, Can. J. Chem. 41 (1963) 770–776.
[29] K.T.I. Yoshihiko, O. Yasuki, Process for Producing Dipentaerythritol, US5254749A (1991).
[30] H.R. Robert, E. John, H. Hasbrouck, Production of Formals of Pentaerythritol, US2464430A (1949).
[31] M. V. V. Daut Vladimir Aleksandrovich, Pojlov Vladimir Zotovich, Pentaerythritol and dipentaerythritol synthesis method, RU2402519C2, 2010.
[32] S. Trybula, K. Terelak, A polish process for pentaerythritol manufacture, Pigm. Resin Technol. 19 (5) (1990) 7–8.
[33] Teng Dongcheng 滕冬成 et al. Method of preparing pentaerythritol and dipentaerythritol, CN101696158B, 2011.
[34] C. Mansson, F. Daniel, Process for production of pentaerythritol with an increased yield of di-pentaerythritol, WO/2020/067963 (2020).
[35] M. Guido Greco, Angelo De Micheli, Saronno, Umberto Soldano, Vittorio Bruzzi, Process for Continuous Manufacture of Pentaerythritol, US3410915A, 1965.
[36] I.I.S.И.И. СаМохвалов, et al., Method of producing pentaerythritol, RU2445303C1 (2012).
[37] Pei Fang 裴丰 et al. Production method for producing pentaerythritol by recycling carbide slag, CN114276214A, 2024.
[38] Wang Jiaxing 王嘉兴 et al. Method for preparing pentaerythritol as well as lithium formate and sodium chloride, CN102115419A, 2011.
[39] Dong Hongwei 邓宏卫 et al. A kind of preparation method of pentaerythritol with co-production sodium oxalate, CN109206297A, 2018.
[40] J.D. Leonard, Process for the recovery of pentaerythritol from crude mother liquors, US3179704A (1960).
[41] H.I. Yalowitz, Recovery of pentaerythritol by formalin extraction, US2780655A (1957).
[42] F. Gupton, et al., Treatment of waste stream from pentaerythritol manufacture, US4612389A (1986).
[43] B.F. Gupton, et al., Byproduct recovery from a pentaerythritol waste stream, US4277620A (1981).
[44] P.E. Eckler, Partial resolution of pentaerythritol waste liquors, US4105575A (1978).
[45] F.M. Lee, Process for treating aldol-condensation polyol waste liquor, US4083931A (1978).
[46] W.O. Snelling, Recovery of valuable products from pentaerythritol mother liquor, US261771A (1952).
[47] A. Heit, Pentaerythritol purification process, US3779883A (1973).
[48] Luo Qiu 罗秋 et al. A kind of Optimized Extraction technique of separating formic sodium, CN106748738A, 2017.
[49] Luo Qiu 罗秋 et al. A kind of packing method of sodium formate product, CN106748736A, 2017.
[50] M.J. Jacobs, Process for refining waste liquor, US4418226A (1983).
[51] Shi Yunhai 施云海 et al. Method for separating and purifying sodium formate from pentaerythritol mother liquor by adopting solid phase extraction-elution crystallization method, CN112745214A, 2022.
[52] Quan Hongdong 全宏冬 et al. Purification method and purification device for pentaerythritol byproduct crude sodium formate, CN111056938A, 2020.
[53] Chen Yongle 陈永乐 et al. Purification method of pentaerythritol byproduct sodium formate, CN115710176A, 2023.
[54] L. Xiaohe, Y. Luqian, L. Hongyan, C. Guanghong, H. Dongdong, R. Jiaqi, W. Lihua, Method for refining 98-grade sodium formate from pentaerythritol mother liquor in one step, CN117736088A (2023).
[55] Liu Qidong 刘启东 et al. Production method of pentaerythritol by virtue of potassium method, CN104447202A, 2016.
[56] Z. Wang, X. Qu, X. Yuan, Z. Gao, N. Hu, J. Wei, W. Li, Z. Yang, J. Wang, Continuous-flow synthesis of pentaerythritol: Alkalinity release of sodium solvation cage to control aldol and Cannizzaro reactions, Chin. J. Chem. Eng. 79 (2025) 23–29, https://doi.org/10.1016/j.cjche.2024.11.005.
[57] Y. Xing, Z. Yan, J. Deng, K. Wang, G. Luo, Efficient Synthesis of Pentaerythritol in a Continuous Microreaction System, Ind. Eng. Chem. Res. 64 (4) (2025) 1983–1993, https://doi.org/10.1021/acs.iecr.4c04497.
[58] Jiang Yuanhua 蒋远华 et al. Method for separating and preparing mono, bis-pentaerythritol and its by-product using high temperature condensation and concatenate recrystallization, CN1736969A, 2009.
[59] Jiang Yuan 蒋 遠 et al. Method for producing pentaerythritol, JP4938773B2, 2012.
[60] Li Yan 李焰 et al. Improved synthesis method of pentaerythritol with low aldehyde ratio, CN117326915A, 2024.
[61] X. Y. J. Yuanhua, B. Pingguan, F. Jiaxin, D. Jinjun, H. Huazhong, L. Yuanhai, Z. Yexiang, H. Leguan, Method of Preparing Pentaerythritol, US8293950B2, 2006.
[62] Xie Tian 解田 et al. Crystallization separation method of pentaerythritol, CN114085127A, 2022.
[63] E. L. T. John C Chmie, Purification of crude pentaerythritol, US3066171A, 1958.
[64] C. Corp, Separation of mixtures of pentaerythritol and dipentaerythritol, GB772574A (1957).
[65] Gwangju Kim 김광주 et al. Purification method of monopentaerythritol by crystallization, KR20050108814A, 2006.
[66] Wang Qiang 王强 et al. The preparation method and the equipment thereof of single, double, three tetramethylolmethane CN1097004A, 1995.
[67] Eck 埃克 et al. Process for preparation of pentaerythritol CN1165804A, 2016.
[68] H.-A. Bengtsson at al. Process for producing monopentaerythritol of high purity and monopentaerythritol produced by the process, US7569736B2, 2009.
[69] Gong Xi 龚喜 et al. Comprehensive utilization method for pentaerythritol production wastewater and formaldehyde acetaldehyde, CN110721554A, 2022.
[70] R. H. Barth, J. E. S. Production of formals of pentaerythritol US2464430A, 1966.
[71] L.G. Maury, et al., Conversion of Pentaerythritol Formals into Pentaerythritol, US2939887A (1957).
[72] Kim Jae-cheol 김재철 et al. The Manufacturing Process of High Purity Pentaerythritol, KR101087217B1, 2011.
[73] Kim Jae-cheol 김재철 et al. The manufacturing process of high purity pentaerythitol, KR20050107322A, 2007.
[74] Zhang Zhengkun 张正坤 et al. High-purity monopentaerythritol purification device, CN218187950U, 2023.
[75] Zhang Zhengkun 张正坤 et al. Device for preparing liquid pentaerythritol from pentaerythritol separation mother liquor, CN218189660U, 2023.
[76] Sun Duolong 孙多龙 et al. Method for preparing 95 grade pentaerythritol, CN104230660A, 2016.
[77] Liu Qidong 刘启东 et al. Production system and production process of 99-grade pentaerythritol, CN109438182B, 2021.
[78] Benkutoshon ベンクトション et al. Method for producing high purity monopentaerythritol, JP5518936B2, 2014.
[79] D.I. Belkin, O.A. Demchenko, A Mathematical Model of the Synthesis of Pentaerythritol, Kinet. Catal. 61 (3) (2020) 374–383, https://doi.org/10.1134/S0023158420030052.
[80] R.Ó. Meadhra, H.J.M. Kramer, G.M. van Rosmalen, Crystallization kinetics of pentaerythritol, J. Cryst. Growth 166 (1) (1996) 1046–1052, https://doi.org/10.1016/0022-0248(96)00113-3.
[81] A. Achour, O. Pajalic, et al., Process for the production of dipentaerythritol, WO2025136213 (2025).