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Review

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Mariia P. Filina[1*], Abdigali A. Bakibaev[1], Farkhad A. Baiguzin[2]

[1]Tomsk State University, Tomsk, Russia;
[2]Engineering-Promotional Center Ingehim, Kazan, Russia
*(*Corresponding author's e-mail: filina@ect-center.com)*

Cyclopentane as an Eco-Friendly Alternative: A Review of its Properties, Industrial Applications, and Production Methods

The Montreal Protocol established stringent international regulations concerning the production, consumption, and trade of ozone-depleting substances, including chlorofluorocarbons and hydrofluorocarbons, aimed at safeguarding the Earth's ozone layer. In this context, cyclopentane has emerged as an environmentally sustainable alternative owing to its zero-ozone depletion potential and low global warming potential. This review examines the physicochemical properties, industrial applications, and production methods of cyclopentane, with particular emphasis on its utilization as a refrigerant, a blowing agent in rigid polyurethane foams, and a hydrate-forming agent for seawater desalination. The primary applications are concentrated in refrigeration and thermal insulation, where cyclopentane-based foams demonstrate superior thermal conductivity and mechanical stability relative to conventional agents. However, the flammability of cyclopentane vapor presents operational challenges that necessitate the implementation of appropriate safety measures. Advances in catalytic reaction-distillation and extractive distillation processes may improve the efficiency of cyclopentane production and product purity in industrial settings. This review underscores cyclopentane's efficacy as a substitute for compounds with higher ozone depletion potentials and emphasizes the importance of ongoing research into scalable, economically viable production technologies and safe industrial integration to fully realize its environmental and practical benefits.

Keywords: cyclopentane, fraction C5, pyrolysis, cyclopentene, cyclopentadiene, hydrogenation, cyclopentane hydrates, eco-friendly

Contents

List of Abbreviations

CPAN:	cyclopentane
CPEN:	cyclopentene

CPD: cyclopentadiene
DCPD: dicyclopentadiene
CFC: chlorofluorocarbons
HFCC: hydrofluorochlorocarbons
HFC: hydrofluorocarbons
ODP: ozone depletion potential
GWP: global warming potential
ORC: Organic Rankine Cycle

Review Plan

Inclusion and Exclusion Criteria: The review is devoted to properties, applications, methods of production cyclopentane.

The review data mostly cover the publications from 1959 to 2025. However, some old literature sources dated on 1925, 1949 are also cited. Articles in the relevant area were searched and analyzed using databases like Scopus, Web of Science, PubMed etc. along with other online scientific search engines (Google Scholar). The keywords used for the search were: «cyclopentane», «blowing agent», «fraction C_5», «pyrolysis», «cyclopentene», «cyclopentadiene», «hydrogenation», «cyclopentane hydrates». No statistical methods were used in this review.

Mariia Filina is a research engineer at the Laboratory of Artificial Intelligence in Chemistry Materials Science at Tomsk State University, Master’s degree in Technological Machines and Equipment from Kazan National Research Technological University. Throughout her scientific and engineering career, she has been involved in a wide range of research fields, including: developing technologies for the synthesis of complex organic compounds, including peroxides, glycosides, and their derivatives; creating technical documentation and engineering solutions related to chemical processing; conducting research on the synthesis and optimization of processes for producing anhydrous hydrogen fluoride and other vital chemicals. She is the author of numerous scientific articles, patents, and technical guidelines related to resource processing, synthetic chemical production, and environmentally sustainable materials.

Abdigali Bakibayev is Professor of Organic Chemistry at Tomsk State University, Doctor of Chemical Sciences. He specializes in the synthesis of biologically active nitrogen-containing compounds, development of new substances from natural raw materials, and chemistry of macro- and supramolecular systems. He has authored over 200 scientific publications, 14 monographs, and more than 50 inventions. His work is applied in industrial production across multiple regions. He actively contributes to scientific and educational communities, serving on dissertation councils and editorial boards, and collaborating internationally, including in Kazakhstan.

Farhad Baiguzin is chemical engineering scientist, PhD (2000). His research interests include applied research in chemical and biochemical engineering. His primary focus areas are heterogeneous catalytic processes, heat and mass transfer, hydrodynamics, and large-scale applications in chemical engineering. He has extensive experience working on various problems as both an employee and head of research at engineering companies. During this period, he co-authored 40 original publications in peer-reviewed journals, including those indexed in Scopus. Additionally, he holds 15 patents for inventions, some of which, when implemented in industry, have generated significant economic impact.

Introduction

The Montreal Protocol [1], which entered into force on 1 January 1989, and its subsequent amendments, established strict measures to regulate the production, export, import, destruction and consumption of ozone-depleting substances — chlorofluorocarbons (CFC), hydrofluorochlorocarbons (HFCC), hydrofluorocarbons (HFC). This agreement played a key role in protecting the Earth's ozone layer and facilitated the transition to safer alternatives.

One alternative to reduce the use of CFC is cyclopentane (CPAN). This hydrocarbon has zero ozone depletion potential (ODP), making it an environmentally friendly choice for use in a variety of industries. In addition, CPAN has a global warming potential (GWP) index of only 5, which is significantly lower than conventional freons.

1 Properties

CPAN is an alicyclic hydrocarbon of composition C_5H_{10} consisting of five carbon atoms joined in a ring. At room temperature it is a colorless very volatile liquid with a petrol smell, has a boiling point of 49.3 °C, melting point of minus 93.9 °C, vapor pressure at 20 °C is 45 kPa and density is 0.745 g/cm^3. Flash point is minus 37 °C, autoignition temperature is 320 °C [2].

CPAN is insoluble in water but mixes well with organic solvents (ethanol, acetone, esters, Stoddard solvent or chlorinated hydrocarbons).

The cyclopentane ring can adopt a flat conformation [3, 4] with little angular strain, since the internal pentagon angle is 108°, which is close to the tetrahedral angle of 109.5°. However, in the flat state, all 10 hydrogen atoms will be shaded, leading to a significant torsional energy of 42 kJ/mol. To avoid this undesirable state, CPAN adopts a lower energy non-planar conformation known as the envelope conformation. This "torsion" occurs due to the rotation of the C–C bonds in the ring.

A few publications are devoted to the calculation of thermophysical properties of CPAN, describing the equation of state, which is expressed through the fundamental thermodynamic Helmholtz energy function. The equation of state for CPAN is presented in the book [5], and the publication [6], an evaluation of the application of the equation is presented in the publication [7], where the errors of the equation for density calculations for the liquid phase at temperatures up to 300 K and above the critical temperature are evaluated. The equation for calculation of thermodynamic properties and phase behavior of cyclic hydrocarbons in the temperature range up to 700 K and at pressures up to 100 MPa is also proposed in [8]. In works [9, 10] the possibility of application for technical calculations of thermophysical properties of CPAN of the NIST REFPROP software product, which is also based on the use of a universal equation of state, is substantiated.

2 Applications

CPAN is not commonly used as a solvent or a raw material for chemical transformations [11], but its ability to efficiently absorb and release heat and minimal GWP defines use as a refrigerant. In works [12–14] the application of CPAN and its mixtures in Organic Rankine Cycle (ORC) is noted. A working fluid with a boiling point lower than water and low viscosity is used as a working body in OCR, which allows efficient conversion of low-potential heat into electricity.

The research [15] analyses efficiency and ecological impact refrigeration compression system of the CPAN in comparison with known freons: tetrafluoroethene (Freon-R134A) and HFC mixtures of R407C and R404A brands. The authors have established that at application of CPAN as a working agent the coefficient of efficiency of the refrigeration cycle made 6.485 at the evaporator temperature of 0 °C and the condenser temperature of 25 °C.

However, the main limitation of CPAN application as a working fluid in household refrigerating appliances is flammability of its vapors (explosion limits [16] from 1.4 % vol. (41 g/m^3) to 8.0 % vol. (233 g/m^3) that creates high level of danger arising at its leaks from the compressor system.

Polyurethane and polyisocyanurate foams using CPAN as a blowing agent are a group of rigid foams that are used as rigid insulation for pipes, inside refrigerated cabinets [17], automotive industry and other areas. Rigid polyurethane foams are most often subjected to compressive rather than tensile loads and sometimes bending or shear stresses. Strength and cell size stability for foams are important.

In Europe, CPAN and its blends have been used like blowing agent for insolation since 1993. CPAN has a lower thermal conductivity (0.0126 W/m-K) than isopentane and *n*-pentane (0.014–0.015 W/m-K) and despite initial concerns about its thermal insulation properties relative to dichlorofluoroethane (CAS 1717-00-6), European appliance manufacturers have found that CPAN-based foams perform better than expected [18].

In respect that the blowing agent capable to migrate in matrix another characteristic of the insulation is its mechanical strength under actual operating conditions. When using CPAN, there is a risk of condensation associated with its high boiling point (49.5 °C), which can reduce the pressure in the cell (up to 0.1 bar at minus 20 °C) and compromise the stability of dimensional and strength of the insulation. These risks have been overcome by increasing the cell molding density in CPAN-based foams [19].

For thermal insulation, ageing prediction is also important, which is based on the research of the diffusion of the foaming agent under storage conditions. Over time, foaming agents migrate into the polyurethane, which affects the mechanical properties of the polymer. Hydrocarbons, including CPAN, diffuse faster than CFCs, but actual diffusion data over 15 years appear to be comparable. The condensate of CPAN in the cells maintains the gas phase concentration. Comparative researches [12] show that although some of the CPAN does dissolve into the insulation material, this does not significantly degrade the compressive strength of the insulation.

The experimental research [20] allowed us to explore the effect of the ratio of CPAN and isopentane on the properties of rigid foams used in the thermal insulation of household appliances. The thermal conductivity of the foam increased from 1.561 to 1.784 W/m-K when going from pure CPAN to a mixture of CPAN : i-pentane = 60:40. The authors also noted changes in the cell size of the obtained foams, with pure CPAN forming smaller cells compared to the mixtures. There are also known works, in particular [21], that focus on the properties of modified foams obtained with the use of CPAN, during the aging period of thermal insulation.

Recently, scientific research has focused on the use of CPAN as a hydrate-forming agent for desalination seawater [22–25]. Cyclopentane hydrates are crystalline compounds formed by interaction of CPAN with water at atmospheric pressure, which makes the use of CPAN in this direction attractive. The process of desalination seawater using cyclopentane hydrates (Figure 1) includes the following steps: mixing of cooled CPAN with salt solution, crystallization — formation of cyclopentane hydrate, separation of hydrates from concentrated solution, heating cyclopentane hydrates and reuse CPAN.

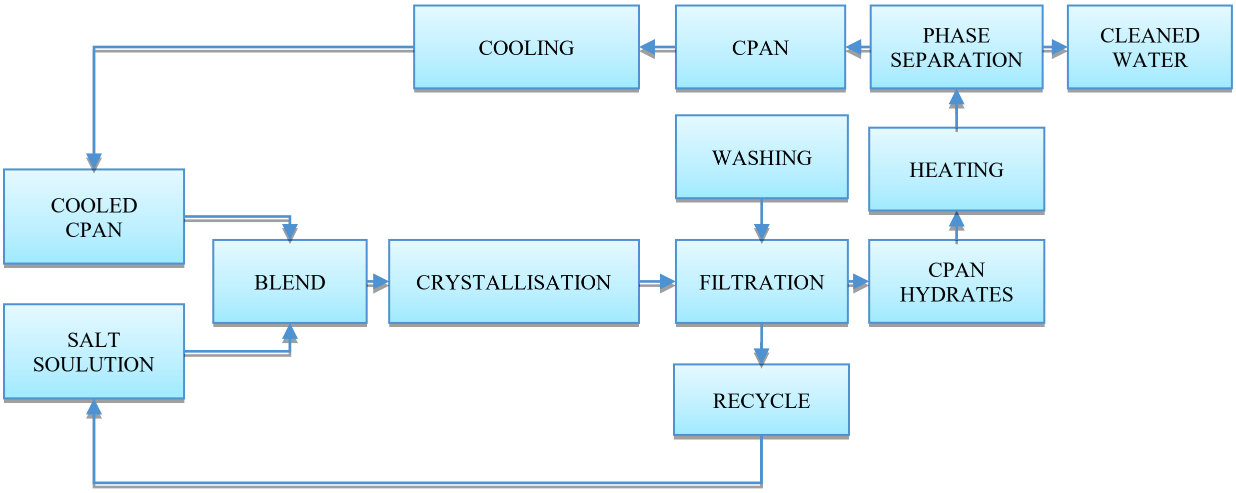


Figure 1. Process of desalination of seawater using cyclopentane hydrates

The review [26] provides a summary of data on hydrate properties, along with a diagram and a desalting process. It should be noted, however, that this process has not yet been implemented on an industrial scale.

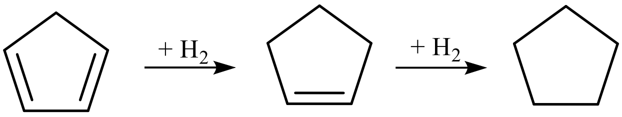
3 Methods of production

CPAN was first obtained by Connor [27] in 1967 by the action of lithium amalgam on dioxane solution of 1,5-dibromopentane in 75 % yield. This method of synthesis is still used in laboratory techniques [28, 29]. A known obsolete laboratory technique [30, 31] is the cyclisation of adipic acid to cyclopentanone which is accompanied by simultaneous dehydration and decarboxylation. To obtain cyclopentanone crystalline adipic acid is heated with barium hydroxide to 285–295 °C at the same time cyclopentanone is slowly distilled off together with a small amount of adipic acid; the ketone is separated from water by calcium chloride or ether extraction, then washed with aqueous alkali, then with water, dried with calcium chloride and distilled with a dephlegmator, collecting the fraction at 128–131 °C; the resulting cyclopentanone is reduced according to Clemmensen in CPAN with zinc amalgam.

CPAN is present in small amounts in oil and gas condensate in fractions with boiling range of 30–60 °C, but obtaining CPAN from oil fractions is hindered by neo-hexane, which has a close boiling point at atmospheric pressure. The objective of the research [32] is to develop a rapid method to select efficient solvents for the separation of CPAN and neo-hexane using extractive distillation. Dimethylformamide was found to be the most suitable of the three solvents tested. Recent research [33] suggests the use of sodium acetate additive to the above solvents to produce high purity CPAN.

The main industrial method of CPAN production is its separation from C_5 hydrocarbon fractions obtained during the pyrolysis process of ethylene production. Light fraction of liquid pyrolysis products contains linear isomeric and cyclic olefins, dienes, and hydrocarbons of acetylene series with the number of carbon atoms from 5 to 8 [34]. Information about the composition of the hydrocarbon fraction of pyrolysis gasoline in the C_5 fraction formed at industrial plants is presented in [35]. The detailed composition of the C_5 hydrocarbon fraction obtained from ethylene units under different reaction conditions is summarized as follows. At EP-60 ($T = 770$ °C, $\tau = 1.3$ s), a longer contact time at a lower temperature result in more complete conversion, with higher contents of alkanes such as isopentane and *n*-pentane, along with a significant proportion of alkenes and alkadienes. At EP-300 ($T = 810$–815 ° C, $\tau = 0.5$–0.6 s), increased temperature and reduced contact time promote intensive dehydrogenation and cracking, decreasing overall C_5 yield and increasing alkynes and cyclic compounds due to extensive dealkylation and cyclization. At EP-450 ($T = 830$ °C, $\tau = 0.4$–0.5 s), even higher temperature and shorter residence time lead to further cracking and aromatization, reducing C_5 yield while increasing the fraction of alkynes and cyclic hydrocarbons. Typically, pyrolysis gasoline contains about 0.5–0.6 wt.% of acetylene hydrocarbons.

The main obstacle of separation CPAN from stream after pyrolysis is azeotrope “1,3-pentadiene-cyclopentene (CPEN)” with boiling point 43.6 °C [36]. Also, as reactive compounds like acetylenes and dienes are the source of polymer formation and limit operations heating and cooling for C_5 fraction of pyrolysis gasoline. Accordingly, in order to extract aromatic and cyclic hydrocarbons, the pyrolysis gasoline is subjected to step-by-step hydrogenation. One of the diolefins present in the C_5 fraction is capable of undergoing complete hydrogenation in CPAN is cyclopentadiene (CPD).



Separation of C_5 hydrocarbons from pyrolysis gasoline is one of way of processing by-products of pyrolysis, which is described in detail in [37, 38]. The generalized essence of the technology, implemented, for example, by the manufacturer Junyuan Petroleum Group [39] is shown in Figure 2.

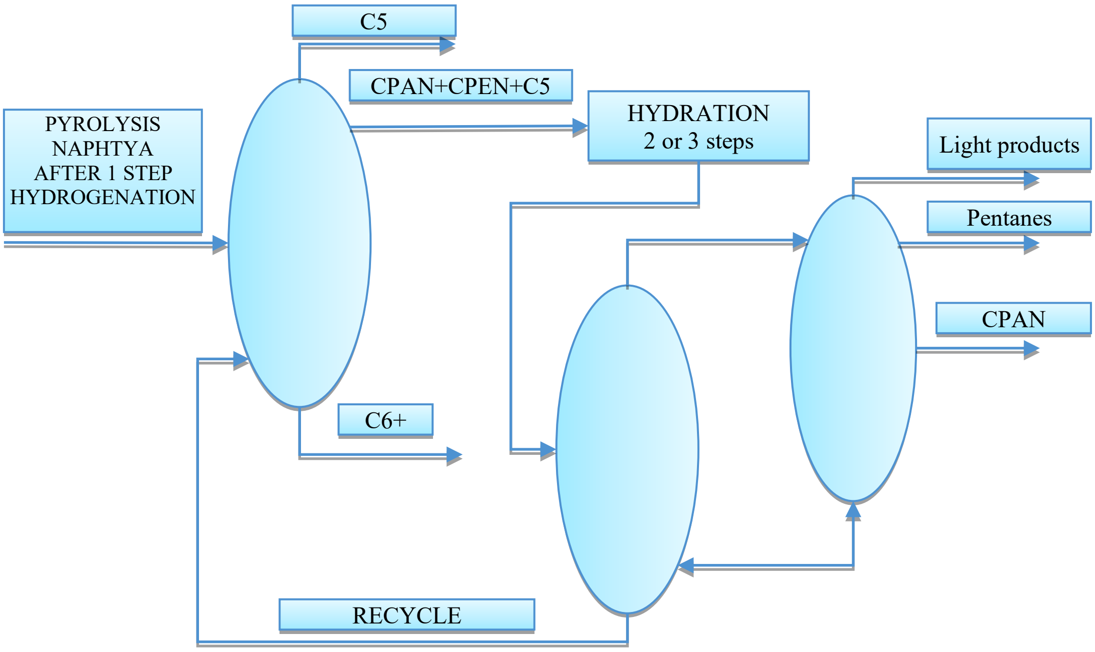


Figure 2. Scheme of CPAN production

One version of technology is also reflected in the patent of BASF AG [40]. The common process technology comprises the following stages: preliminary hydrogenation of pyrolysis naphtha to remove diene hydrocarbons and alkynes, separation of the enriched CPAN-CPEN fraction from hydrogenation naphtha, and separation of CPAN, normal and isopentanes, heavy return products and dissolved light products in rectification columns.

Haltermann Carless GmbH [41], the world's largest producer of CPAN, has an annual production capacity of approximately 100,000 tons. The unit is capable of producing hydrogenated CPAN and middle distillates, normal and isopentane. It can also produce individual hydrocarbons by separating them in the period rectification unit.

A similar approach is applied in Rosneft's patent [42] and other publications [43–47], which differ in terms of the sequence of primary and final hydrogenation stages, stream fractionation, as well as application of extractive methods of mixture separation in some cases.

An alternative way to obtain CPAN with purity up to 99 % is hydrogenation of CPD, which can be obtained from coal tar in the form of its dimer — dicyclopentadiene (DCPD) in the amount of about 10–20 g per tons of coal [48] or from the C_5 fraction of pyrolysis gasoline, which is treated to obtain DCPD [49]. The storage and transportation of CPD occurs in the form of a DCPD dimer.

There are a number of steps involved in the process of separating DCPD from the C_5 fraction. In a first step, C_5 fraction heating the at normal pressure and a temperature of 30–100 °C for 5–24 hours or at elevated pressure and a temperature of 140–150 °C and CPD is dimerized into DCPD. In a second step, the remaining components of the fraction with a boiling point of 28–50 °C are distilled off and 85–90 % crude DCPD is obtained at the bottom of the column. In the third step, the crude DCPD by monomerization to give cyclopentadiene with a purity of about 95 % [50]. After monomerization CPD hydrogenation yields CPEN according to the Bayer method [51] or used an alternative scheme for obtaining isoprene and CPEN from the C_5 fraction using extractive distillation with N-methyl pyrrolidone [52].

The review of literature devoted to methods of hydrogenation of CPD allows us to highlight several works [53–56]. It should be noted that the process of hydrogenation of CPD to CPEN is well studied and described in detail in various publications [53, 57], the interest in the research of this reaction is determined by the possibility of using CPEN as a monomer for the synthesis of frost-resistant rubbers and other polymers used for optoelectronics [58]. CPD is easily hydrogenated to CPAN on nickel catalyst in alcoholic solvents at 25 °C and atmospheric pressure [59]. The catalytic hydrogenation and isomerisation of various linear and cyclic mono- and diolefins as well as aromatic compounds using the diphenylphosphinomethylhydride compound $[Cp_2ZrH(CH_2PPh_2)]_n$ with respect to CPD, the hydrogenation reaction to CPEN and CPAN is shown in [60].

Another way to carry out hydrogenation of CPD using the heat released during the chemical transformation of CPD into CPAN is realized in [54]. This approach is developed in [61, 62] by realizing the process of CPAN production in reaction-distillation apparatuses. Publications on the process of producing CPAN from DCPD via combined reaction-distillation processes are relatively scarce and are primarily documented in patent literature. For instance, one patent [62] describes the production of CPAN in a single catalytic distillation column, which integrates the functions of cracking DCPD, hydrogenation of CPD, and separation of hydrogenation products. In this process, DCPD and hydrocarbons are fed into the lower part of the catalytic column, where cracking to CPD occurs. Hydrogen is also introduced at the bottom of the column to hydrogenate the formed CPD during its distillation. The result is a vapor stream of CPAN, which condenses and is collected as a liquid product. Concurrently, continuous product separation takes place: CPAN is withdrawn as the top distillate, while heavy by-products remain as bottom residue.

A similar procedure for producing CPEN from DCPD is described in another patent [63]. Here, the process is carried out in a reaction-distillation apparatus with the catalytic system located directly within the packing layer of the apparatus. Thus, the primary scheme for producing CPAN from DCPD described in the literature involves feeding the raw materials into the hydrogenation zone along with a vapor stream, with continuous liquid irrigation by condensed products, as depicted in Figure 3.

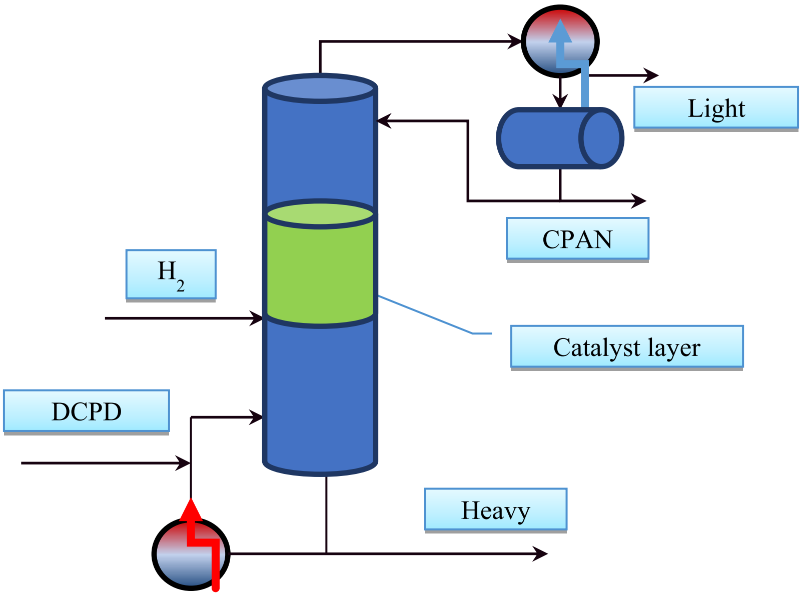


Figure 3. Scheme of CPAN production in reaction-distillation process

It should be noted that in spite of available variants of realization of technology of CPAN production and apparent efficiency of separation methods at industrial realization it is necessary to take into account a number of economic factors, often determining profitability of future production. In particular, special attention should be paid to provision of production with raw materials and possibilities of shipment of finished products. Taking into account the territorial dispersion of pyrolysis plants and, accordingly, the sources of C_5 fraction required in production, in some cases it is reasonable to consider the use of concentrated dimer of CPD as a raw material for processing.

Conclusions

The extensive industrial utilization of cyclopentane in widely manufactured products, coupled with its growing significance in innovative applications such as seawater desalination via cyclopentane hydrates, provides strong impetus for developing novel industrial production methods and identifying alternative raw material sources for large-scale cyclopentane synthesis. Presently, industrial cyclopentane production predominantly depends on the fractionation of petroleum-derived streams boiling within the 30 to 60 °C range. Advances in catalyst technology and process optimization continue to improve both yield and product purity.

Conventional hydrogenation of pyrolysis gasoline fractions yields cyclopentane; however, additional production opportunities exist through processing dicyclopentadiene from the C_5 pyrolysis fraction isolating. These considerations highlight the need for ongoing research and development focused on catalyst design, integration of reaction-distillation processes, and extractive separation techniques. Such efforts are essential to establish economically viable and scalable industrial processes capable of producing cyclopentane from a variety of way.

*Author Information**

**The authors' names are presented in the following order: First Name, Middle Name and Last Name*

Mariia Petrovna Filina (*corresponding author*) — Engineer, Tomsk State University, Lenin Ave., 36 634050, Tomsk, Russia; e-mail: filina@ect-center.co; https://orcid.org/0009-0001-2808-1661

Abdigali Abdimanapovich Bakibaev — Doctor of Chemical Sciences, Professor, Tomsk State University, Lenin Ave., 36 634050, Tomsk, Russia; e-mail: bakibaev@mail.ru; https://orcid.org/0000-0002-3335-3166

Farkhad Abdriaufovich Baiguzin — Candidate of Technical Sciences, Engineer, Engineering-Promotional Center Ingehim LLC, 14/83 Shalyapin Str., 420049, Kazan, Russia; e-mail: umns_inform@rambler.ru; https://orcid.org/0009-0007-4251-9117

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Abdigali Abdimanapovich Bakibaev** conceptualization, methodology, validation; **Mariia Petrovna Filina** visualization, writing-original draft, writing-review & editing data curation, formal analysis; **Farkhad Abdriaufovich Baiguzin** formal analysis, validation, writing editing.

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Declaration of Generative AI and AI-Assisted Technologies in the Writing Process

During the preparation of this work the authors used Grammarly in order to refine the language of the manuscript. After using this service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

Conflicts of Interest

The authors declare no conflict of interest.

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