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## REVIEW OF 5-HMF SYNTHESIS: CATALYSIS AND TECHNOLOGIES



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**Abstract.** 5-Hydroxymethylfurfural (5-HMF) is recognized as a key platform molecule in the bioeconomy, serving as a precursor for the production of biofuels (2,5-dimethylfuran, 5-ethoxymethylfurfuryl ether), biopolymers (2,5-furandicarboxylic acid), and pharmaceutical intermediates. This review systematizes modern approaches to the synthesis of 5-HMF from carbohydrate feedstocks of varying complexity – from monosaccharides (fructose, glucose) to cellulose and lignocellulosic biomass (rice straw). Catalytic systems (homogeneous acids, ionic liquids, heterogeneous catalysts, including functionalized silica gel  $\text{SiO}_2\text{-Imi-SO}_3\text{H}$  and sulfated zeolite  $\text{HSO}_3\text{-ZSM-5}$ ), solvent effects (dimethyl sulfoxide, biphasic water/organic solvent systems, including dichloromethane/tetrahydrofuran), process intensification methods (ultrasound, microwaves), and strategies for suppressing side reactions are analyzed in detail. The main pathways of 5-HMF chemical transformation are discussed, along with techno-economic and environmental aspects of production based on life cycle assessment (LCA) and bibliometric analysis. Key challenges (catalyst and separation costs, stability) and promising research directions (low-cost bifunctional catalysts, deep eutectic solvents, process integration, electrochemical methods, use of non-food biomass) are identified.

**Keywords:** 5-hydroxymethylfurfural (5-HMF), biomass, carbohydrate dehydration, fructose, glucose, cellulose, ionic liquids, heterogeneous catalysts, biphasic systems, platform molecules, renewable feedstocks, biofuels, furandicarboxylic acid (FDCA).

## ОБЗОР 5- ГМФ СИНТЕЗА: КАТАЛИЗ И ТЕХНОЛОГИИ

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**Аннотация.** 5-Гидроксиметилфурфурол (5-ГМФ) признан ключевой платформенной молекулой в биоэкономике, служащей предшественником для производства биотоплива (2,5-диметилфурана, 5-этоксиметилфурфуролового эфира), биополимеров (2,5-фурандикарбоновой кислоты) и фармацевтических промежуточных продуктов. В данном обзоре систематизированы современные подходы к синтезу 5-ГМФ из углеводного сырья различной сложности - от моносахаридов (фруктозы, глюкозы) до целлюлозы и лигноцеллюлозной биомассы (рисовой соломы). Подробно проанализированы каталитические системы (однородные кислоты, ионные жидкости, гетерогенные катализаторы, включая функционализированный силикагель  $\text{SiO}_2\text{-Imi-SO}_3\text{H}$  и сульфатированный цеолит  $\text{HSO}_3\text{-ZSM-5}$ ), эффекты растворителей (диметилсульфоксид, двухфазные системы воды/органических растворителей, включая дихлорметан/тетрагидрофур), методы интенсификации процессов (ультразвук, микроволны)

и стратегии подавления побочных реакций. Обсуждаются основные пути химического превращения 5-ГМФ, а также технико-экономические и экологические аспекты производства на основе оценки жизненного цикла (ОЖЦ) и библиометрического анализа. Определены ключевые проблемы (стоимость катализатора и сепарации, стабильность) и перспективные направления исследований (низкозатратные бифункциональные катализаторы, глубинные эвтектические растворители, интеграция процессов, электрохимические методы, использование непищевой биомассы).

**Ключевые слова:** 5-гидроксиметилфурфурол (5-ГМФ), биомасса, дегидратация углеводов, фруктоза, глюкоза, целлюлоза, ионные жидкости, гетерогенные катализаторы, двухфазные системы, платформенные молекулы, возобновляемые сырьевые материалы, биотопливо, фурандикарбоновая кислота (ФДКА).

## 5-HMF SINTEZI SHARHI: KATALIZ VA TEXNOLOGIYALAR

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**Annotatsiya.** 5-Gidroksimetilfurfurol (5-GMF) bioyoqilg'ilar (2,5-dimetilfuran, 5-etoksimetilfurfuril efir), biopolimerlar (2,5-furankarbon kislotasi) va farmatsevtik oraliq mahsulotlar ishlab chiqarish uchun prekursor sifatida xizmat qiladigan bioiqtisodiyotda asosiy platforma molekulasini sifatida tan olingan. Ushbu sharhda turli murakkablikdagi uglevod xom ashyosidan - monosaxaridlardan (fuktoza, glyukoza) sellyuloza va lignotsellyuloza biomassasigacha (sholi somoni) 5-GMF sinteziga zamonaviy yondashuvlar tizimlashtirilgan. Katalitik tizimlar (gomogen kislotalar, ionli suyuqliklar, geterogen katalizatorlar, shu jumladan funkcionallashtirilgan silikagel  $\text{SiO}_2$ -Imi- $\text{SO}_3\text{H}$  va sulfatlanagan seolit  $\text{HSO}_3$ -ZSM-5), erituvchilar ta'siri (dimetilsulfoksid, ikki fazali suv/organik erituvchilar tizimlari, shu jumladan dixlormetan/tetragidrofuran), jarayonlarni jadallashtirish usullari (ultratovush, mikroto'liqlar) va qo'shimcha reaksiyalarni bostirish strategiyalari batafsil tahlil qilingan. 5-GMF ni kimyoviy o'zgartirishning asosiy yo'llari, ishlab chiqarishning texnik-iqtisodiy va ekologik jihatlari hayotiy siklni baholash (TSB) va bibliometrik tahlil asosida muhokama qilinadi. Asosiy muammolar (katalizator va ajratish xarajatlari, barqarorlik) va istiqbolli tadqiqot yo'nalishlari (arzon bifunksional katalizatorlar, chuqur evtektik erituvchilar, jarayon integratsiyasi, elektrokimyoviy usullar, nooziq-ovqat biomassasidan foydalanish) aniqlangan.

**Kalit so'zlar:** 5-gidroksimetilfurfurol (5-GMF), biomassa, uglevodlar degidratatsiyasi, fuktoza, glyukoza, sellyuloza, ion suyuqliklar, geterogen katalizatorlar, ikki fazali tizimlar, platforma molekulasini, qayta tiklanadigan xomashyolar, bioyoqilg'ilar, furankarbon kislotasi (FDKK).

**Introduction.** The transition from fossil resources to renewable feedstocks is a central challenge for the sustainable development of the chemical industry in the 21st century [1, 2]. In this context, 5-hydroxymethylfurfural (5-HMF) stands out as one of the most promising platform molecules, identified both by the U.S. National Laboratories and the European Bioeconomy Platform [3]. Its unique structure, combining aldehyde, hydroxyl, and furan functional groups, makes 5-HMF a versatile building block for the synthesis of a wide range of valuable products [3, 4, 5]. Catalytic reduction of 5-HMF yields liquid biofuels such as 2,5-dimethylfuran (DMF) and 5-

ethoxymethylfurfuryl ether (EMF), which are competitive with conventional gasoline in terms of energy density [6, 7]. Oxidation of 5-HMF produces 2,5-furandicarboxylic acid (FDCA), regarded as an environmentally friendly alternative to terephthalic acid in the production of polyethylene furanoate (PEF) – a biopolymer with outstanding barrier properties [8, 9, 10]. The annulated furan ring of 5-HMF also serves as a basis for the synthesis of diverse heterocyclic compounds used in pharmaceuticals and fine organic synthesis [3, 5, 11].

Despite its significant potential, large-scale industrial production of 5-HMF still faces serious

challenges [2, 12]. The key issues include:

1. Selectivity and yield: The need to minimize complex side reactions (formation of humins, levulinic acid, and formic acid) [13, 14, 15];

2. Feedstock base: Economic feasibility and sustainability of using food-derived sugars (fructose) vs. the potential of non-food lignocellulose [16, 17, 18];

3. Catalysts: The search for highly active, selective, stable, and regenerable catalytic systems that combine availability with environmental safety [2, 19, 12];

4. Separation and purification: High energy demand and cost of isolating 5-HMF from reaction mixtures, particularly aqueous systems [20, 21, 22];

5. Scaling up: Transition from laboratory methods to pilot and industrial-scale plants [23, 24].

The aim of this review is to provide a systematic analysis of recent advances in the synthesis of 5-HMF from renewable carbohydrate feedstocks, with a focus on developed catalytic systems (including promising heterogeneous catalysts), technological aspects (choice of solvent, extraction, process intensification), utilization of complex biomass, as well as an evaluation of economic and environmental prospects based on up-to-date data. Special attention is given to recent studies that reflect current research trends.

**Feedstock for 5-HMF Synthesis.** The success of 5-hydroxymethylfurfural (5-HMF) synthesis largely depends on the choice of raw material, which is typically carbohydrates with varying degrees of polymerization. The simplest and most efficient route is to use monosaccharides, such as fructose, which can be easily converted into 5-HMF with high yields. At the same time, more abundant and cheaper feedstocks, such as polysaccharides (e.g., cellulose), require additional steps: first, hydrolysis to break down complex polymers into simple sugars (mainly glucose), followed by their conversion into 5-HMF. Thus, the choice of feedstock represents a compromise between high efficiency (with fructose) and economic feasibility (with cellulose) [25, 26, 27].

**Monosaccharides. Fructose:** Considered the optimal feedstock due to its ketohexose structure, which readily undergoes dehydration. Yields of 5-HMF from fructose in dipolar aprotic solvents (DMSO) with acid catalysts can reach 90–96% [28,

29, 21, 30]. The dehydration mechanism involves consecutive steps of enolization, dehydration, and cyclization [14, 30, 63]. However, the high cost of food-grade fructose limits its industrial application. Low-temperature synthesis methods of 5-HMF from fructose, developed in [31], improve the energy efficiency of the process.

**Glucose:** As the primary monomer of cellulose, glucose is economically attractive. However, efficient conversion to 5-HMF requires prior isomerization into fructose [32]. This additional step reduces the overall 5-HMF yield (typically to 50–70%) and complicates the process [33, 34]. The key lies in developing bifunctional catalysts (e.g., Sn- $\beta$  [48], HSO<sub>3</sub>-ZSM-5 [17]) that combine Lewis acid sites (for isomerization) and Brønsted acid sites (for dehydration).

**Disaccharides and Polysaccharides.** Sucrose (glucose + fructose) and inulin (a fructose polymer) can also serve as feedstocks but require preliminary hydrolysis into monosaccharides [27]. Oligosaccharides formed during partial hydrolysis of cellulose are also of interest.

**Cellulose.** Direct conversion of cellulose to 5-HMF is a challenging task due to its crystallinity, the stability of  $\beta$ -1,4-glycosidic bonds, and its tendency to form side products. Yields rarely exceed 30% [25, 35, 36, 37, 38, 39, 40]. The most successful approaches include:

- Use of ionic liquids (ILs) as solvents and catalysts (e.g., with CrCl<sub>3</sub>) [35, 41, 42];
- Combined systems with strong Lewis acids (e.g., metal chlorides) in ILs or water at elevated temperatures [36, 38, 41];
- Application of solid acids (sulfated zirconia SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>, zeolites) in biphasic media [19, 43].

**Lignocellulosic Biomass.** The use of non-food biomass (agricultural residues, wood, energy crops) is the most promising direction in terms of sustainability and economics [16, 17, 18, 44]. However, its complex composition (cellulose, hemicellulose, lignin) requires multi-step processing:

- **Pretreatment:** Physical (milling), physico-chemical (steam explosion, AFEX), or chemical (acidic, alkaline, oxidative) methods to break down lignin and hemicellulose and increase cellulose

accessibility [17, 45];

- *Cellulose hydrolysis*: A key step in obtaining 5-HMF from biomass, aimed at breaking long cellulose chains into simpler sugars, primarily glucose. This can be achieved in two main ways [17, 32]: by enzymatic hydrolysis, using specific enzymes such as cellulases and hemicellulases, or by chemical hydrolysis, catalyzed by dilute acids. The former is more environmentally friendly but slower, while the latter is faster but requires harsher conditions and careful control to prevent glucose degradation into byproducts;

Table 1

**Comparison of the efficiency of converting various feedstocks into 5-HMF**

Feedstock	Catalyst/System	Catalyst/System	5-HMF Yield, %	Ref.
Fructose	[C <sub>4</sub> C <sub>1</sub> im][HSO <sub>4</sub> ] (IL)	IL, 120 °C, 30 min	96	[29]
Fructose	SiO <sub>2</sub> -Imi-SO <sub>3</sub> H	DMSO, 160 °C, 4 h	94.1	[46]
Glucose	Al <sub>2</sub> O <sub>3</sub> в [C <sub>4</sub> C <sub>1</sub> im]Cl	IL, 120 °C, 3 h	70	[33]
Glucose	HSO <sub>3</sub> -ZSM-5	DMSO, 140 °C, ultrasound-assisted	54.1	[17]
Glucose	Sn-β	Water, 160–190 °C	~50 (ЛНТ.)	[32]
Cellulose	CrCl <sub>3</sub> в [C <sub>4</sub> C <sub>1</sub> im]Cl	IL, 140 °C, 2 h	62	[41]
Cellulose	Hafnol phosphate	Biphasic (water/MIBK), 180 °C, 5 h	52	[43]
Rice straw	HSO <sub>3</sub> -ZSM-5 (+ cellulase, pretreatment)	Water, 140 °C, ultrasound-assisted (multistep)	54.1	[17]
Кукурузная Corn stover	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> in IL	IL, 140 °C, 2 h	45	[47]

**Catalytic conversion:** Isomerization of glucose and dehydration of the resulting fructose into 5-HMF [17]. Combining hydrolysis and dehydration in a single “one-pot” process is an active area of research. An example of successful

implementation is the conversion of rice straw with a 54.1% 5-HMF yield after alkaline pretreatment, enzymatic hydrolysis, and HSO<sub>3</sub>-ZSM-5 catalysis under ultrasound [17].

*Note:* Ultrasound-assisted (UA) – ultrasonic treatment; IL – ionic liquid; DMSO – dimethyl sulfoxide; MIBK – methyl isobutyl ketone; lit. – literature data.

**Catalytic Systems.** The catalyst plays a crucial role in determining the selectivity and efficiency of carbohydrate dehydration to 5-HMF. Research has focused on overcoming the limitations of traditional systems and developing highly efficient, stable, and regenerable catalysts [2, 12, 19, 61].

**Homogeneous Catalysts.** *Mineral acids (H<sub>2</sub>SO<sub>4</sub>, HCl, H<sub>3</sub>PO<sub>4</sub>):* They are highly active and readily available. The yield of 5-HMF from fructose in DMSO can reach 89% [48]. However, they have significant drawbacks: strong corrosiveness, difficulties with regeneration and reuse, formation of large amounts of by-products (humins, levulinic acid), especially in aqueous media, and the need for neutralization that generates salt wastes [13, 15, 48]. The kinetics of 5-HMF degradation into levulinic acid are well documented [13].

*Organic acids (levulinic, oxalic, p-toluenesulfonic acid):* Considered a more “green” alternative to mineral acids due to lower corrosivity and, in some cases, better selectivity [7]. However, their activity is often lower and costs are higher.

*Ionic liquids (ILs):* These are salts that are liquid below 100 °C. They have proven to be exceptionally effective media and catalysts (especially chlorometallate ILs, e.g., with CrCl<sub>3</sub>, AlCl<sub>3</sub>) for the conversion of fructose (yields up to 96% [29]), glucose (up to 70% [33]), and even cellulose (up to 62% [41]). Key advantages include low volatility, high solubilizing ability for biomass, good thermal stability, and tunable acid–base properties [29, 35, 40, 41, 49, 60]. Critical drawbacks that limit industrial application are high viscosity, challenges in regeneration and product purification, potential toxicity of certain ILs, and above all, very high cost [12, 29, 35].

**Heterogeneous Catalysts.** This is a rapidly developing research area since heterogeneous catalysts potentially overcome the drawbacks of homogeneous systems: they can be easily separated



from the reaction mixture, regenerated, and reused [12, 17, 19, 32, 34, 43, 46, 47, 50, 51, 65].

**Acidic resins and zeolites:** Ion-exchange resins (e.g., Amberlyst) are effective for fructose dehydration, especially in organic solvents or biphasic systems [49]. Zeolites (protonated and modified forms) are attractive due to their structure, thermal stability, and tunable acidity. Sulfonated zeolite HSO<sub>3</sub>-ZSM-5 has proven to be an efficient bifunctional catalyst for glucose and real biomass (rice straw) conversion with yields up to 54.1%, maintaining activity due to ultrasound-assisted treatment that enhances mass transfer [17].

**Functionalized mesoporous materials:** These are designed to introduce active sites on high-surface-area supports (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, carbon). An example is SiO<sub>2</sub>-Imi-SO<sub>3</sub>H, synthesized by immobilizing a sulfonated ionic liquid fragment on silica gel [46]. It combines strong Brønsted acidity (from IL) with the operational benefits of a heterogeneous catalyst. In DMSO, it provides a 94.1% yield of 5-HMF from fructose at 160 °C within 4 h and retains >85% activity after 5 regeneration cycles. Its properties were confirmed by IR spectroscopy, XRD, TGA, and EDS analysis [46].

**Sulfated metal oxides (SO<sub>4</sub><sup>2-</sup>/M<sub>x</sub>O<sub>y</sub>):** These exhibit strong Brønsted acidity and high thermal stability. They are effective for fructose and glucose dehydration (SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>) [19, 34, 47, 64]. SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> in IL achieved a 45% 5-HMF yield from corn stover [47].

**Metal-based heterogeneous catalysts:** Catalysts containing Sn, Cr, Al, Zr, Ga, or Fe often provide Lewis acid sites, which are essential for glucose isomerization. Sn-β zeolite shows high selectivity in converting glucose to fructose and subsequently to 5-HMF in water [32]. Chromium-based systems (e.g., Cr phosphates, Cr on supports) are also active, but issues of Cr leaching and toxicity need to be addressed [50, 43]. The use of Pd catalysts on mesoporous zirconosilicates for hydrogenation of 5-HMF and its derivatives has also shown promising results [52].

**Phosphates and other salts:** Metal phosphates and hydrogen phosphates (e.g., of cerium, zirconium, hafnium) have delivered good results in biphasic systems. Hafnium phosphate enabled a 52% 5-HMF yield from cellulose in a water/MIBK

biphasic system [43].

Table 2  
**Comparison of main types of catalysts for 5-HMF synthesis**

Catalyst Type	Example	Main Advantages	Main Disadvantages	Feedstock (Yield)	Ref.
Homogeneous acids	H <sub>2</sub> SO <sub>4</sub>	High activity, low cost	Corrosion, difficult regeneration, salt wastes	Fructose (89%)	[48]
Ionic liquids	[C <sub>4</sub> Sim][HSO <sub>4</sub> ]/CrCl <sub>3</sub>	High yield, low volatility, dissolves cellulose	High viscosity, very high cost, Cr toxicity	Fructose (96%), Cellulose (62%)	[29], [41]
Acid resins	Amberlyst-15	Easy separation, regeneration	Limited thermal stability	Fructose (high)	[49]
Sulfated oxides	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub>	Strong Brønsted acidity, thermal stability	Possible SO <sub>4</sub> <sup>2-</sup> leaching	Glucose (moderate), Biomass (45%)	[47], [34]
Functionalized materials	SiO <sub>2</sub> -Imi-SO <sub>3</sub> H	High activity/selectivity, stability, regenerable	Relatively complex synthesis	Fructose (94.1%)	[46]
Zeolites (bifunctional)	HSO <sub>3</sub> -ZSM-5	Bifunctionality (Lewis + Brønsted), regenerable, ultrasound-stable	Moderate activity with glucose	Glucose (54.1%), Biomass (54.1%)	[17]
Metal-containing	Sn-β	High selectivity for glucose isomerization, "green" catalyst	Moderate dehydration activity, synthesis complexity	Glucose (~50%)	[32]
Metal phosphates	Hafnium phosphate	Effective in biphasic systems with cellulose	High Hf cost	Cellulose (52%)	[43]

### Technological Aspects of Synthesis

**Role of Solvents.** Water as a solvent in the oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) has limited application due to its role in side reactions. The presence of water in the reaction medium promotes the hydration of HMF, leading to the cleavage of the furan ring and the formation of levulinic and formic acids. This undesirable pathway actively competes with the main reaction, reducing selectivity to below 50% and making the process economically inefficient and purification-intensive. For this reason, researchers are exploring alternative solvents less prone to hydration to improve yields, as discussed in [13, 14].

In the production of HMF from fructose, dimethyl sulfoxide (DMSO) as a solvent allows high yields of up to 94.1% [28, 30]. This is because DMSO, unlike water, is an aprotic solvent that does not participate in undesired hydration side reactions of fructose or HMF. However, despite its efficiency, DMSO presents two significant drawbacks: difficulties in product separation due to the similar polarity of HMF and DMSO, and the toxicity of the solvent itself, which makes the process less

environmentally friendly and challenging for industrial scale-up.

Biphasic systems such as dichloromethane/tetrahydrofuran (DCM/THF) have been effectively applied to HMF synthesis. Their main advantage is that HMF generated in the aqueous phase is immediately extracted into the organic phase, preventing decomposition and polymerization. This continuous removal of product from the reaction zone (according to patent EP3424914A1) [1] shifts the equilibrium toward HMF formation, enabling >90% extraction efficiency and significantly improving overall yields, compared to homogeneous aqueous systems where HMF undergoes side reactions, as discussed by Binder J.B. and Raines R.T. (2009) [20, 21].

Ionic liquids such as  $[C_4C_{1im}][HSO_4]$  act as highly efficient solvents and catalysts for HMF production. They allow impressive yields up to 96% [29, 41, 60], significantly higher than those obtained in aqueous media. This is attributed to their ability to stabilize intermediates and suppress side reactions such as hydration and polymerization. However, their industrial application remains limited due to high viscosity, which hinders mixing, heat and mass transfer, as well as product separation and solvent recycling, making the process technically complex and expensive.

**Process Intensification.** Ultrasound is used to improve HMF yields from rice straw. Ultrasonic irradiation increases yields by 15–20%, primarily by de-agglomerating biomass particles [17]. This process breaks down large straw aggregates, increasing the surface area accessible to catalysts and solvents, thereby enhancing reaction efficiency and improving conversion of raw material to HMF.

Microwave irradiation provides another route for intensifying HMF synthesis. Its main advantage is rapid and uniform heating of the reaction mixture from within, drastically reducing reaction times from hours to minutes. This makes the process more efficient and cost-effective. For example, microwave-assisted conversion of straw achieves yields of 50–60% [45], demonstrating that microwaves not only accelerate the process but also enable acceptable yields even from complex biomass feedstocks. The fast, controlled heating minimizes side reactions typical of prolonged conventional heating and helps preserve HMF.

Microreactors represent a modern approach for HMF production, offering precise control over reaction conditions. Unlike conventional large-scale reactors, microreactors have very small volumes, enabling accurate regulation of temperature, pressure, and residence time. Such precision significantly enhances process selectivity by minimizing undesired byproducts such as humins or levulinic acid, ultimately improving HMF yields [53].

**Suppression of Side Reactions. Strategies:** Reaction time control is one of the key approaches for efficient HMF synthesis. Optimal reaction times typically range from 30 to 120 minutes [13]. If too short, the feedstock (e.g., fructose or biomass) does not fully convert to HMF, lowering yields. If too long, HMF, being unstable, degrades via hydration into levulinic acid or polymerizes into humins, which reduces yields and complicates purification.

Use of phase modifiers (e.g., NaCl) in biphasic systems enhances HMF extraction and reduces its residence time in the aqueous phase [22].

In situ extraction is a critical method to address HMF instability in aqueous media. The principle is that freshly formed HMF in the aqueous phase is immediately extracted into an immiscible organic phase, minimizing contact with water. This prevents degradation into side products such as levulinic acid and substantially increases overall yields, as confirmed, for example, by the Avalon Industries AG patent (EP3424914A1) [20].

Table 3  
*Selected chemical transformations of 5-HMF and their applications*

Product	Synthesis Method	Application	Yield (%)	Reference
2,5-Dimethylfuran (DMF)	Hydrodeoxygenation over Pt-Co/C	Biofuel (energy density $\approx 30$ MJ/L)	>90	[6]
FDCA (2,5-Furandicarboxylic acid)	Oxidation over Pt/Au catalysts	Biopolymers (PET alternative)	85–95	[8, 10]
5-Ethoxymethylfurfural (EMF)	Etherification with $H_2SO_4$	Diesel fuel additive	>90	[7]

**Pharmaceuticals.** The synthesis of heterocycles for anti-inflammatory drugs [5, 11]. Wittig reactions using 5-HMF enable the formation of furan-2-enones, which are considered promising intermediates for pharmaceutical applications [54].

### Techno-Economic Analysis

**Bibliometric Data.** In recent years, there has been a noticeable shift in scientific research: after 2010, 72% of all publications focused on heterogeneous catalysts. This is not accidental. Unlike “liquid” catalysts that mix with the product and are difficult to separate afterwards, heterogeneous catalysts are solid substances. They can be easily removed from the reaction mixture and reused. Such an approach makes production not only cheaper but also more environmentally friendly, since it reduces waste generation and allows valuable materials to be recycled multiple times [2, 44].

In recent years, the United States and China have taken leading positions in research related to heterogeneous catalysts. According to available data, the United States accounts for about 550 scientific papers, while China accounts for 500 [44]. This indicates that these countries are key players in the development of new, more efficient, and environmentally friendly catalysts for the chemical industry.

### Key Economic Barriers

**Raw material costs.** The cost price of the final product directly depends on the price of the feedstock. For example, the use of expensive fructose (\$500–700 per ton) leads to a high production cost of 5-HMF (over \$2000 per ton). At the same time, switching to low-cost feedstock, such as rice straw (\$50–100 per ton), can reduce the cost to \$800–1200 per ton [18, 24].

**Separation costs.** Product purification and separation from the reaction mixture represent one of the most expensive stages. Separation costs can reach 60–70% of total capital expenditures due to the complexity of the process and the need to isolate pure 5-HMF, as well as recycle the catalyst and solvent [12, 30].

**Catalyst stability.** The efficiency and economics of production directly depend on the catalyst’s lifetime. For example, the  $\text{SiO}_2\text{-Imi-SO}_3\text{H}$  catalyst loses 15% of its activity after just 5 cycles [46], which requires frequent regeneration or replacement, thereby increasing overall costs.

### Environmental Assessment (LCA)

**Emission reduction.** The production of 5-HMF from biomass is a more environmentally friendly process compared to petrochemical routes.

It allows for a 40–60% reduction in carbon dioxide ( $\text{CO}_2$ ) emissions, contributing to climate change mitigation [18].

**Environmental risks.** Despite its advantages, the process is not without drawbacks. Some catalysts, for example those containing chromium (Cr), are toxic. Their use requires strict safety measures. In addition, the release of solvents such as dimethyl sulfoxide (DMSO) into water bodies may lead to eutrophication — rapid algae growth that harms aquatic ecosystems [24, 62].

### Conclusion and Perspectives

#### Achievements:

**Bifunctional catalysts.** Researchers have developed new, highly efficient catalysts such as  $\text{HSO}_3\text{-ZSM-5}$  and  $\text{SiO}_2\text{-Imi-SO}_3\text{H}$ . They are called “bifunctional” because they can perform two tasks simultaneously: first hydrolyzing complex polysaccharides (e.g., cellulose) into simpler sugars, and then converting these sugars into 5-HMF. This approach has significantly increased 5-HMF yields from cellulose, reaching over 50% [4, 7].

**Optimization of biphasic systems.** Biphasic systems such as dichloromethane (DCM)/tetrahydrofuran (THF) have also been improved. These systems consist of two immiscible liquids. The 5-HMF formed in one phase is immediately transferred to the other, organic phase. This helps protect 5-HMF from decomposition and polymerization, ultimately increasing product yield and purity [20].

#### Challenges:

The economic feasibility of 5-HMF production remains questionable if the product yield is below 60%. At low yields, most of the valuable feedstock is consumed in the formation of unwanted byproducts, making the process unprofitable.

Another serious problem is the degradation of catalysts under real operating conditions. Many catalysts that show excellent results in laboratory tests quickly lose their activity and stability during prolonged use or when working with complex feedstocks such as biomass. This requires frequent replacement or costly regeneration, increasing operational costs.

#### Future directions:

**1. Catalysts.** To reduce toxicity and production costs, researchers propose replacing expensive and harmful chromium (Cr)- and tin (Sn)-



based catalysts with safer and cheaper zeolites based on iron and aluminum (Fe/Al) [19, 38]. These new catalysts are not only economically advantageous but also less toxic, making the overall process greener.

2. *Solvents*. To avoid environmental risks associated with toxic solvents such as DMSO, safer alternatives are proposed, such as  $\gamma$ -valerolactone ( $\gamma$ -VL) [12]. This solvent is considered “green” since it is biodegradable and does not cause eutrophication of water bodies, unlike DMSO.

3. *Integrated biorefineries*. Integration of several stages into a single continuous process is another promising strategy. Instead of first synthesizing 5-HMF and then separately converting

it into 2,5-furandicarboxylic acid (FDCA), these stages can be combined into so-called integrated biorefineries [8, 24]. This approach significantly improves overall process efficiency, reduces costs, and minimizes waste.

*Electrochemical methods*. The development of electrochemical methods opens new opportunities for the synthesis of 5-HMF and its derivatives. This technology enables selective oxidation at room temperature [4], which is a huge advantage. Traditional methods often require high temperatures and pressures. The electrochemical approach is more energy-efficient and allows for more precise reaction control, minimizing the formation of byproducts.

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