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Towards efficient furfural production: A review of biphasic solvent systems for enhanced yields and industrial scalability

Kritsana Namhaed[1], Worapon Kiatkittipong[1,2], Patrick Cognet[3], Vesna Najdanovic-Visak[4], Tetsuya Kida[2,5,6], Armando T. Quitain[2,7], and Suttichai Assabumrungrat[8,9]*

[1] Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand
[2] International Research Organization for Advanced Science and Technology (IROAST), Kumamoto University, Kumamoto 860-8555, Japan
[3] Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Université de Toulouse, Toulouse 31062 Cedex 9, France
[4] Chemical Engineering and Biotechnologies, Energy & Bioproducts Research Institute, Aston University, Birmingham B47ET, United Kingdom
[5] Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan
[6] Institute of Industrial Nanomaterials (IINa), Kumamoto University, Kumamoto 860-8555, Japan
[7] Center for International Education, Kumamoto University, 2-40-1 Kurokami, Chuo Ward, Kumamoto 860-8555, Japan
[8] Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
[9] Bio-Circular-Green-economy Technology & Engineering Center (BCGeTEC), Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

***Corresponding author**:*
Worapon Kiatkittipong
kiatkittipong_w@su.ac.th

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ABSTRACT

Furfural, a valuable platform chemical with wide industrial applications, has been produced for decades. Renewed interest in biorefinery processes has driven efforts to improve its production and expand industrial applications. However, challenges in achieving high furfural yield and purity after recovery remain significant bottlenecks. Coupling the reaction with simultaneous separation has emerged as a promising approach, with biphasic solvent systems gaining significant research attention. This review consolidates recent progress in using organic solvents within biphasic systems for furfural production from both simple sugars and raw biomass, covering both homogeneous and heterogeneous catalytic systems, as well as batch and continuous operation modes. Key topics include the formation and mechanisms underlying biphasic systems, which provide insights for process design, and an analysis of factors influencing furfural yields, aiding in reaction optimization. Strategies to enhance process efficiency-such as solvent selection and tuning, phase ratio adjustment, catalyst stabilization, and integration into continuous-flow systems-are discussed in detail. The impact of these strategies on catalytic performance and furfural selectivity is highlighted, along with a techno-economic analysis showing a promising minimum selling price. Finally, this review addresses the opportunities, challenges, and limitations associated with advancing furfural production in biphasic solvent systems.

Keywords: biphasic system; catalysis; extraction; furfural; organic solvent

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1. INTRODUCTION

In the current transition from traditional chemistry to more sustainable practices, often called “green chemistry”, the focus is increasingly on producing bio-based products, recycling waste, promoting a circular economy, and conserving natural resources. This change is driven by concerns about dwindling fossil fuel reserves and growing environmental issues, pushing industries to reduce their reliance on petroleum-based materials and embrace renewable alternatives (Kunkes et al., 2008). In this context, lignocellulosic biomass is seen as a sustainable raw material due to its renewable nature, abundance, and wide availability in nature. It is primarily made up of three components: hemicellulose, cellulose, and lignin (Dodds & Gross, 2007; Vispute et al., 2010). Hemicellulose, the second most common polysaccharide in plant cell walls, makes up about 19-34% of lignocellulosic biomass (Yousuf et al., 2020). Its amorphous structure makes it easier to hydrolyze compared to crystalline cellulose, yielding mainly C5 monosaccharides like xylose (pentoses). Xylose has gained significant attention as it can be converted into various valuable chemicals, including furfural and its derivatives, which have been highlighted in recent reviews (Dashtban et al., 2012; Eseyin & Steele, 2015; Machado et al., 2016; Delbecq et al., 2018).

Furfural, also known as furfuraldehyde, is recognized as one of the top 10 high-value bio-based chemicals (Bozell & Petersen, 2010). It is in high demand and widely utilized across various industries, including oil refining for lubricants and biofuels, plastics for resins and synthetic fibers, pharmaceuticals, and agrochemicals for herbicides, fungicides, and insecticides. Additionally, it serves as a flavoring agent in the food industry (Bhogeswararao & Srinivas, 2015). The production of furfural has garnered significant attention from researchers, leading to a substantial increase in related publications over the past decade (Figure 1). However, despite this growing interest, the number of review articles on furfural production remains relatively limited, as illustrated in Figure 1.

To date, no synthetic method exists for producing furfural in the chemical industry. Its production relies solely on the acid-catalyzed dehydration of C5 sugars derived from hemicellulose (Yang et al., 2012a; Namhaed et al., 2024a). The industrial production of furfural dates back to 1921 when Quaker Oats developed a process involving the acid-catalyzed hydrolysis of hemicellulose, followed by the dehydration of pentosans from lignocellulosic materials (Brownlee & Miner, 1948). The yield from commercial furfural production, based on the pentosan content of the feedstock, was about 40–50% w/w of the theoretical maximum yield of 72.7% w/w (Kamm et al., 2013). The low yield was largely due to unwanted side reactions, such as condensation between furfural and xylose or its intermediates, resinification, and furfural decomposition or fragmentation (Yan et al., 2014). To improve furfural yield and selectivity, it is crucial to quickly extract the furfural from the reaction mixture to prevent its degradation through secondary reactions (Yang et al., 2013).

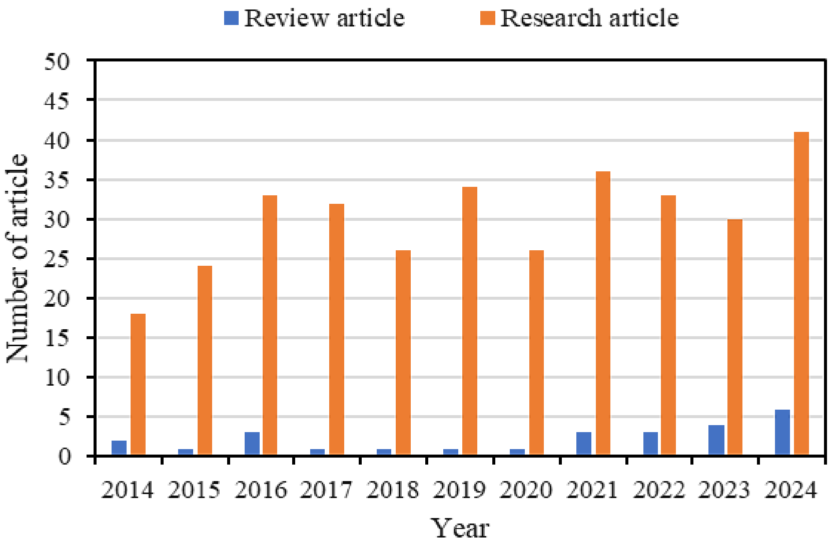


Figure 1. Publications regarding furfural production over the last ten years in the Scopus database, based on the search term “furfural production” in the title, abstract, and keywords, and filtered to include only research articles and reviews

Current approaches to furfural production aim to minimize side reactions in the liquid phase. Four common extraction methods used in furfural production include steam stripping, nitrogen (N_2) stripping, supercritical carbon dioxide, and organic solvents in biphasic systems (Dulie et al., 2021). Research articles detailing furfural production using each of these extraction methods are presented in Figure 2. Among these methods, organic solvent biphasic systems have received the most research attention and are regarded as highly promising by the scientific community. Although many studies focus on furfural production using biphasic solvent systems, review papers specifically dedicated to this topic are limited, as summarized in Table 1.

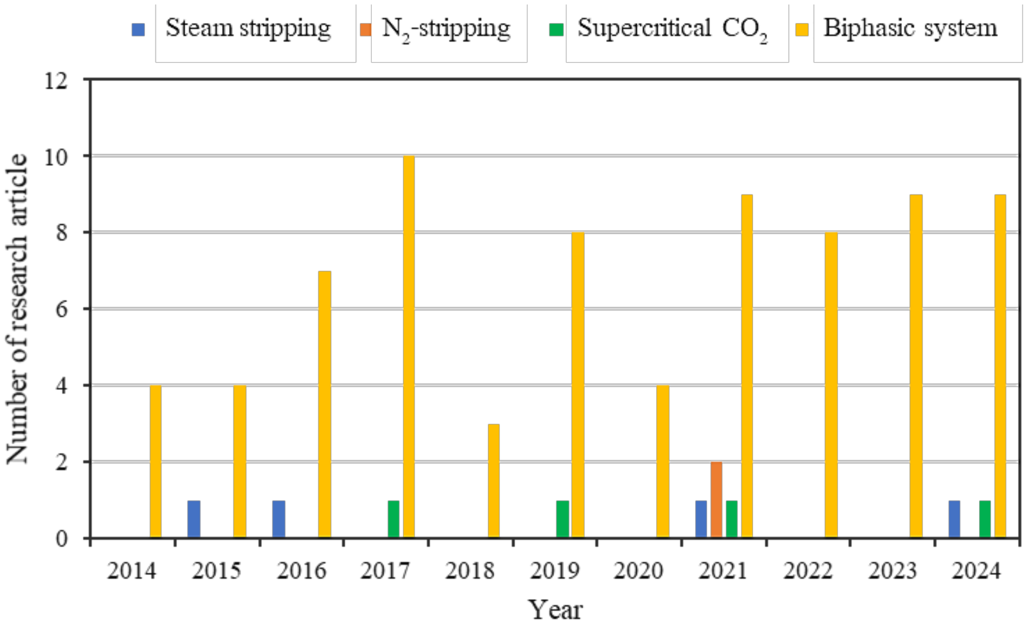


Figure 2. Number of research articles on furfural production using various extraction methods over the last ten years, based on data from the Scopus database

Note: The data represents individual searches combining the term "furfural production" with keywords for each method: "steam stripping"; "N_2-strpping" or "nitrogen stripping"; "supercritical CO_2" or "supercritical carbon dioxide"; "biphasic". The search was applied to titles, abstracts, and keywords, and the results were filtered by document type to include only research articles.

The most recent review, published in 2024, titled "Innovative Biphasic Solvent Systems for Lignocellulosic Biorefinery", provides an overview of the latest advances in biphasic solvent systems for enhancing the production of liquid fuels and furan-based compounds, including furfural and 5-HMF, in lignocellulosic biorefineries. While that review focuses on the use of different organic solvents, it does not address the effects of operating parameters or catalyst types on the production of furan-based compounds in biphasic systems. Our review aims to address this gap by outlining the key parameters influencing furfural production, including operating conditions and the production process, and emphasizing the advantages of biphasic systems compared to mono-aqueous production systems. It then evaluates the benefits and limitations of various catalyst systems within biphasic setups. Additionally, the economic feasibility of furfural production in biphasic solvent systems is reviewed. Finally, the paper explores the challenges associated with scaling up biphasic solvent systems and identifies future directions for their applications in large-scale furfural production.

2. METHODOLOGY OF REVIEW

This review was conducted with the objective of synthesizing current knowledge on furfural production using biphasic solvent systems and evaluating their comparative advantages over other extraction methods. To ensure comprehensive coverage, more than 120 peer-reviewed publications from 2014 to early 2024 were surveyed using databases such as Scopus and Web of Science. Search keywords included "furfural production", "biphasic solvent system", "steam stripping", "supercritical CO_2", and "catalyst for furfural".

From this initial pool, 70 studies focusing specifically on biphasic systems were selected for detailed analysis. An additional 10 studies covering alternative extraction methods (steam stripping, nitrogen stripping, and supercritical CO_2) were also reviewed for comparative purposes. Studies were chosen based on relevance, data completeness, and experimental comparability. Key evaluation criteria included reaction performance (conversion, yield, selectivity), catalyst type and reusability, solvent stability and recovery, process scalability, and economic metrics (e.g., minimum selling price, production cost). Comparative analysis was structured around process conditions (temperature, residence time, solvent selection), catalytic mechanisms (homogenous vs. heterogenous), and by-product formation. Figures 1 and 2 were used to identify publication trends and dominant extraction strategies, which informed the formulation of this review's central research questions: (i) what are the critical factors influencing furfural yield and selectivity in biphasic systems? (ii) how do different catalysts and solvents impact reaction efficiency and sustainability? (iii) what are the techno-economic and scalability challenges in implementing biphasic systems at an industrial scale?

The synthesis of these findings allowed for a structured comparison across systems. In particular, biphasic solvent systems were found to consistently offer higher furfural yields and purities by facilitating in situ extraction, which reduces side-product formation. Techno-economic assessments reported in multiple studies (e.g., Dulie et al., 2021; Namhaed et al., 2025) suggest that biphasic systems can achieve lower production costs when optimized, primarily due to improved solvent recyclability and lower degradation losses. These insights not only confirm the advantages of biphasic systems but also contribute to the development of a theoretical framework linking solvent selection, reaction environment, and furfural production efficiency in biorefinery contexts.

Table 1. Review papers on furfural production involving simultaneous solvent extraction

Year	Title	Main focuses	References
2012	Production of furfural: overview and challenges	- Various processes which have been developed for producing furfural from woody biomass, agricultural residues, and commercially available sugars. - Challenges and technical problems associated with laboratory- and commercial-scale furfural production processes.	(Dashtban et al., 2012)
2020	An insight into the valorization of hemicellulose fraction of biomass into furfural: Catalytic conversion and product separation	- Insights and understanding of lignocellulosic biomass conversion over various catalysts in view of the production of furfural. - Reaction mechanisms, pretreatment methods to enhance furfural yield and the various catalysts. - Furfural isolation mechanisms.	(Dulie et al., 2021)
2020	An overview of the biphasic dehydration of sugars to 5-hydroxymethylfurfural and furfural: A rational selection of solvents using COSMO-RS and selection guides	- Solvents employed for the reaction followed by in situ extraction of these two furans in liquid–liquid systems.	(Esteban et al., 2020)
2021	A review on solvent systems for furfural production from lignocellulosic biomass	- Advantages and limitations of each solvent system	(Lee & Wu, 2021)
2021	Recent progress in furfural production from hemicellulose and its derivatives: Conversion mechanism, catalytic system, solvent selection	- Preparation technology of furfural by catalytic hydrolysis - Reaction mechanism, catalytic system and the solvent system of furfural synthesis using hemicellulose and its derivatives xylan and xylose as raw materials.	(Ye et al., 2021)
2022	Furfural production from biomass residues: Current technologies, challenges and future prospects	- Insights and strategies for improving furfural production using the solid catalysts and simultaneous extraction	(Yong et al., 2022)
2022	Towards efficient and greener processes for furfural production from biomass: A review of the recent trends	- Recent trend towards efficient and greener processes for furfural production from biomass. - Process improvements via pretreatment, improvements in the chemical routes including innovative catalysts, selection of solvents, and the use of activation techniques.	(Cousin et al., 2022)
2024	Innovative biphasic solvent systems for lignocellulosic biorefinery	- Recent advances in the development of biphasic solvent systems in lignocellulosic biorefinery for improving the production of liquid fuels and furan-based compounds	(Cai et al., 2024)

3. FURFURAL PRODUCTION AND ITS DEGRADATION

To date, no synthetic method for producing furfural has been available in the chemical industry (Yang et al., 2012a; Cousin et al., 2022). Furfural is typically derived from lignocellulosic biomass by dehydrating pentosans, primarily xylan, which is abundant in the hemicellulose of various agricultural residues. The main production pathway involves two steps: first, the pentosan sugars in hemicellulose are hydrolyzed to yield xylose, which is then dehydrated to produce furfural. In addition to xylose, arabinose, the second most abundant pentose in biomass, can also be dehydrated to form furfural. However, arabinose is less reactive than xylose due to the different spatial arrangement of its hydroxyl groups (Garrett & Dvorchik, 1969). The overall reaction is expressed as follows :

$$(C_5H_8O_4)_n + nH_2O \rightarrow n(C_5H_{10}O_6) \rightarrow n(C_5H_4O_2) + 3nH_2O$$

Pentosanes *n-pentoses* *furfural*

The theoretical yield of furfural is 72.7% w/w from pentosan and 64% w/w from pentose, calculated on a weight basis (Zeitsch, 2000).

The first step of furfural production proceeds rapidly with a high yield (Mansilla et al., 1998). However, the second step is much more complex due to the occurrence of side reactions. These can be grouped into two main categories: resinification, where furfural undergoes self-polymerization, and condensation, where furfural cross-polymerizes with intermediates from the xylose-to-furfural conversion. The latter results in the formation of black, insoluble carbonaceous substances known as humins. Additionally, fragmentation reactions also occur, further reducing the yield of furfural (Jing & Lü, 2007) (Figure 3). The main byproduct of furfural degradation is formic acid, which is produced through the hydrolysis of the aldehyde group in furfural (De Jong & Marcotullio, 2010). To minimize these side reactions, furfural must be continuously extracted from the reaction medium during production.

To illustrate the efficiency of lignocellulosic biomass utilization for furfural production on various scales, including commercial and laboratory setups, a mass balance for furfural production based on 100 kg of raw lignocellulosic biomass is depicted in Figure 4. Following pretreatment, four main components are obtained: solid cellulose, hemicellulose liquor, solid lignin, and ash, as described by Haq et al. (2021). The hemicellulose, serving as the starting material for furfural production, is decomposed into hexose and pentose sugars, with pentose comprising the majority (90% w/w) (Börjesson et al., 2019).

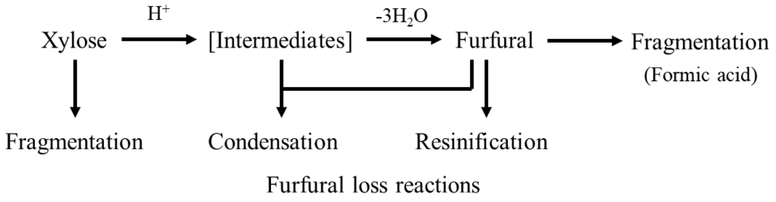


Figure 3. Simplified scheme of the possible reactions in the xylose-to-furfural process

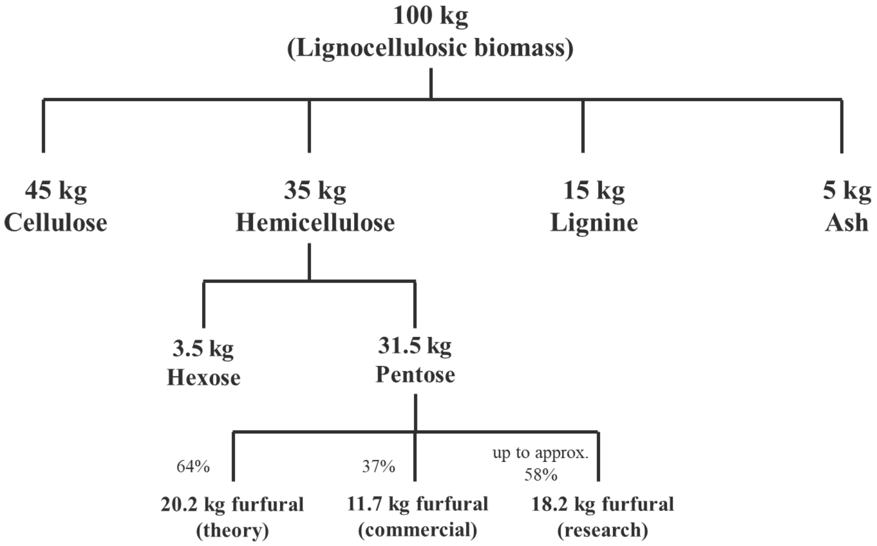


Figure 4. Mass balance of furfural production from lignocellulosic biomass
Note: The mass percentages of various components in lignocellulosic biomass used for the calculations were obtained from Haq et al. (2021), while the hexose and pentose content in the hemicellulose fraction was sourced from Börjesson et al. (2019).

Furfural yields from commercial production (Kamm et al., 2013) are significantly lower than the theoretical value. This shortfall is largely attributed to side reactions during processing, underscoring the importance of simultaneous extraction techniques to enhance yields. Despite the lower yields, the furfural obtained from commercial processes typically exhibits high purity. For example, the Westpro-modified Chinese Huaxia Furfural Technology achieves a furfural purity of 98.5% with yields ranging from 35–50% (Win, 2005). In contrast, research studies (e.g., Sener et al., 2018; Zhang et al., 2021) have shown that yields close to the theoretical value can be attained by incorporating simultaneous extraction techniques. However, most research efforts focus solely on the production stage without progressing to the recovery of pure furfural. As a result, the purity remains unverified and cannot be compared to that of commercial production, despite the higher yields. To ensure consistency and facilitate comparisons across studies, furfural yields in the subsequent sections of this review are expressed as molar percentages, the standard unit in related literature.

4. BIPHASIC SOLVENT SYSTEM FOR ENHANCED FURFURAL PRODUCTION

Four common extraction methods for recovering furfural from the reaction medium include steam stripping, N_2-stripping, supercritical CO_2 extraction, and the use of organic solvents in biphasic systems. The advantages and drawbacks of each method are summarized in Table 2. Among these processes, the use of organic solvents in biphasic systems stands out as the most promising, offering significant benefits over other methods. Specifically, biphasic systems avoid the formation of azeotropic mixtures, simplifying the recovery of pure furfural, and enable continuous extraction of furfural from the aqueous phase, thereby suppressing side reactions and improving both yield and selectivity. In addition to their technical advantages, biphasic systems require lower energy input compared to steam or N_2-stripping and do not demand the high pressures associated with supercritical CO_2 setups. They also allow for easier catalyst separation and solvent recyclability, making them more compatible with continuous processing systems and attractive for industrial replication. Although the use of organic solvents necessitates proper volatile organic compounds (VOCs) management, their operational simplicity, scalability, and cost-effectiveness reinforce their suitability for industrial-scale furfural production. Moreover, this extraction method is the most extensively studied approach within the scientific community, as previously mentioned. Consequently, this review paper focuses on biphasic solvent systems for furfural production. The details of the advantages of biphasic solvent systems are discussed in the following section.

4.1 Formation and mechanism of a biphasic solvent system

The use of a biphasic system, consisting of an aqueous phase and an organic phase, offers a promising approach to improving furfural production. In this system, once furfural is formed in the aqueous phase, it is immediately extracted into the organic phase due to furfural's higher affinity for the organic solvent. This continuous extraction process helps prevent furfural from undergoing degradation reactions, which typically occur in the aqueous phase where the catalysts are present (Zhang et al., 2018). Mechanistically, vigorous stirring at high speed disperses the reactive solution into the organic solvent. Each droplet of the aqueous phase functions as a mini-reactor where furfural is produced and immediately transferred to the organic phase (Figure 5). This maintains a low concentration of furfural in the aqueous phase, reducing the likelihood of side reactions and ensuring higher selectivity (Rong et al., 2012).

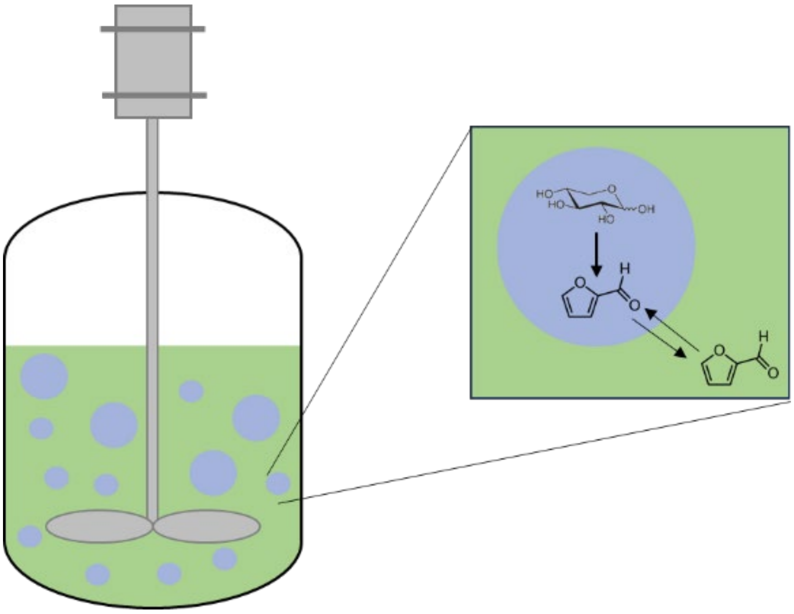


Figure 5. Scheme of biphasic solvent system for furfural production, illustrating the reaction in the aqueous phase (blue) and the continuous extraction of the furfural product into the organic phase (green).

Table 2. Comparative analysis of furfural extraction methods – principles, advantages, and drawbacks

Method	**Principle**	**Typical temp. (°C)**	**Reaction time (h)**	**Reactor type**	**Advantages**	**Drawbacks**	**Environmental impact consideration / Green features**	**References**
Steam stripping	Formation of low-boiling furfural-water azeotrope	170–200	1–2	Semi-batch reactor	- Ease of manipulation	- Very high energy consumption: large steam input required - High cooling needs for stripping vapors - Azeotropic separation of furfural/water mixture necessary	- High carbon footprint unless coupled with renewable steam generation or heat recovery systems	(Yang et al., 2013; Kamm et al., 2013; Sadhukhan et al., 2014)
N_2-stripping	High diffusivity of N_2	160–180	1–2.5	Semi-batch or continuous reactor (typically fixed-bed with N_2 sparging)	- Inert, easily separable and recyclable gas - Lower energy requirements than steam stripping - High product purity - Easy catalyst separation	- High equipment costs: recompression of N_2 and large vacuum unit required	- Lower energy use vs. steam - No solvent waste - Recyclable N_2 minimizes waste gas emissions	(Agirrezabal-Telleria et al., 2012; Dulie et al., 2021)
Supercritical carbon dioxide (Sc-CO_2)	High diffusivity of Sc-CO_2	35–140	0.5–4	High-pressure semi-batch reactor	- Chemically inert, non-flammable - Easy recycling and separation from the product - Acts as a catalyst by acidifying the system - Low temp (<50°C)	- Safety: high-pressure operation - High equipment costs due to pressure support - Complexity requires specialized training	- CO_2 can be recycled and reused - No organic solvents - Low thermal energy needed	(Sako et al., 1992; Sangarunlert et al., 2007; Namhaed et al., 2024b)
Biphasic solvent system	Good affinity with organic solvent	140–200	0.5–6	Batch or flow reactor	- Avoidance of azeotropic separation of furfural/water - Simplified catalyst and product separation	- Some solvents may be toxic or volatile (risk of VOCs) - Costly if solvent not recycled	- Use of green solvents (e.g., CPME, GVL) reduces toxicity - Solvent recovery essential to minimize environmental burden	(Mariscal et al., 2016; Namhaed et al., 2025)

4.2 Factors influencing furfural production

Selecting an appropriate solvent system is an effective strategy in biphasic systems to enhance the selectivity of furfural, as it directly influences both the thermodynamics and kinetics of the reaction. Additionally, the reaction conditions, such as the aqueous phase to organic phase volume ratio and the stirring velocity, must be optimized based on the specific characteristics of the solvent system being used. Proper tuning of these parameters is crucial for maximizing furfural extraction efficiency, minimizing degradation, and ensuring high yield and selectivity in biphasic systems (Luo et al., 2019; Zhao et al., 2021).

4.2.1 Solvent type

To avoid undesired side reactions, a suitable solvent for furfural extraction must possess key properties, including a high partition coefficient for furfural, low mutual solubility with water, good chemical stability, and resistance to forming an azeotrope with furfural (Lin et al., 2015). Various solvents used as organic phases in biphasic systems for furfural production are outlined in Table 3.

Among various solvents, toluene has been the most commonly-used extraction solvent in biphasic systems due to its high partition coefficient for furfural and low solubility in water (Agirrezabal-Telleria et al., 2012; Rong et al., 2012; Mittal et al., 2017). In 2012, Rong et al. (2012) developed a method to produce furfural from xylose at atmospheric pressure using sulfuric acid (H_2SO_4) as a catalyst and NaCl as a promoter. By using toluene as the organic extraction solvent, they achieved a maximum furfural yield of 83% in a biphasic system. Qing et al. (2017) also reported a successful biphasic system with toluene as the extraction layer, which improved furfural yield from pre-hydrolyzed corncob liquor and raw corncob using a SO_4^{2-}/SnO_2-MMT solid catalyst. In a pure water phase, the furfural yield was 43.71% with a xylose conversion of 91.08%. In contrast, the water/toluene biphasic system improved furfural yield to 48.27%, while solvents like methyl isobutyl ketone (MIBK) and γ-valerolactone (GVL) showed no significant improvement in furfural yield when used with the SO_4^{2-}/SnO_2-MMT catalyst system.

Although toluene has a strong affinity for furfural and low solubility in water, it is highly toxic. Therefore, environmentally friendly renewable solvents have been introduced as replacements to align with the principles of green chemistry and sustainable development. Ethyl butyrate (EB) was tested as a renewable alternative to toluene at elevated temperatures. A furfural yield of 75% was achieved after 3 h at 200°C in an EB/water system. More recently, Gómez Millán et al. (2021) assessed furfural production from xylose under auto-catalyzed conditions using a biphasic system with water-immiscible solvents such as isophorone, 2-methyltetrahydrofuran (2-MTHF), and cyclopentyl methyl ether (CPME). Of these, CPME produced the highest furfural yield at 78% with a 93% selectivity at a 1:1 organic solvent-to-water ratio. In a biphasic system using a 1:1 mass ratio of MIBK to aqueous xylose solution, xylose dehydration to furfural in acidic media (0.1 M HCl) achieved over 80% yield under optimal conditions-double the yield of a single-phase aqueous system. Kinetic studies revealed that introducing an extracting solvent in a biphasic system did not fundamentally change the kinetic parameters compared to a monophasic system. However, it was observed that the decomposition rate of xylose increased, and higher furfural concentrations accumulated in the organic layer (Weingarten et al., 2010). To minimize furfural losses in the aqueous phase—caused by phase equilibrium as the rate of product formation slows down during the reaction—a continuous system with a constantly replenished extracting phase would be necessary. This approach could enhance furfural yield by efficiently removing the product as it forms.

4.2.2 Ratio of aqueous phase to organic phase

Besides the properties of the organic solvent, the ratio of the aqueous to organic phases is a key factor that significantly influences extraction efficiency and, consequently, furfural selectivity in biphasic systems (Aellig et al., 2015; Papaioannou et al., 2019).

Yang et al. (2013) demonstrated that the volume percentage of the extracting solvent, o-nitrotoluene, significantly affected both furfural yield and selectivity. As the volume of o-nitrotoluene increased from 0% to 80%, the furfural yield rose from 30% to 70%, and selectivity improved from 70% to 99%. Similar trends were observed by Gómez Millán et al. (2019) when isophorone, 2-MTHF, and CPME were used as extraction agents. Insufficient volumes of the extracting phase led to saturation, limiting the transfer of furfural from the aqueous phase, where it underwent degradation reactions. Wang et al. (2019a) observed that excessive organic solvents, such as 2-MTHF, reduced the activity of $FePO_4$ catalytic sites in the aqueous phase. This led to a decrease in furfural yield from 84% to 65% when the organic-to-aqueous phase volume ratio increased from 1:1 to 3:1. Conversely, excessive water lowered the partition coefficient of the reaction system and promoted furfural rehydration, further reducing the yield (Qing et al., 2017). The partition coefficient of the system was found to be 10.3 at a 1:4 volume ratio of 2-MTHF to NaCl-water, significantly lower than the 18.8 observed at a 1:1 ratio. Optimizing the ratio of aqueous to organic phases is crucial for maximizing furfural extraction efficiency. Insufficient organic solvent can impede extraction, while excessive solvent increases production costs and complicates downstream separation and recovery processes. Achieving an optimal balance is essential for minimizing both economic and operational challenges in industrial applications.

4.2.3 Reaction temperature

In industrial monophasic batch and continuous furfural production processes, an increase in temperature generally improves the conversion of xylose into furfural. However, higher temperatures also accelerate competing side reactions that degrade furfural, resulting in reduced yields (Gao et al., 2014). Kinetic studies reveal that the activation energy (E_a) for these side reactions is higher than that for xylose conversion into furfural. For example, Namhaed et al. (2024a) found that in a monophasic batch system catalyzed by formic acid, the E_a for the cross-polymerization side reaction was 200.80 kJ/mol, compared to 156.04 kJ/mol for xylose conversion. Similarly, Lamminpää et al. (2012) observed an E_a of 235.0 kJ/mol for the cross-polymerization side reaction, significantly higher than the 155.0 kJ/mol for xylose conversion. These findings highlight that elevated temperatures disproportionately accelerate side reactions relative to xylose conversion, emphasizing the importance of optimizing temperature to balance the rates of production and degradation, thereby achieving high furfural yield and selectivity.

Table 3. Biphasic solvent system for furfural production from simple sugars and raw biomass

System	Temp. (°C)	Time		Substrate	Solvent	Catalyst	Yield (%)	Number of runs	*Yield (%)	References
		Residence time	Time on stream							
Simple sugars										
Batch	100	5h	-	Xylose	Water/toluene	H_2SO_4, NaCl	83	-	-	(Rong et al., 2012)
	140	3h	-	Xylose	Water/DCM	HCl	79	-	-	(Chheda et al., 2007)
	140	1h	-	Xylose	Water/THF	$AlCl_3.6H_2O$/NaCl	75	3	73	(Yang et al., 2012b)
	150	10 min	-	Xylose	Water/acetone	H_3PO_4	54	-	-	(Wang et al., 2018)
		45 min			Water		42			
	180	15 min	-	Xylose	Water/MIBK	$FeCl_3$	76	5	75	(Zhang et al., 2021)
	190	3h	-	Xylose	Water/2-sec-butylpnol	-	59	-	-	(Gómez Millán et al., 2021)
	120	3h	-	Xylose	Water/toluene	Nb_2O_5	72	4	70	(Gupta et al., 2017)
					Water		48		42	
	120	4h	-	Xylose	Water/MIBK	ChCl	75	1	69	(Jiang et al., 2018)
	130	2h	-	Xylose	Water/GVL	FeClx/1-D008	96	4	90	(Sun et al., 2021)
	140	6h	-	Xylose	Water/toluene	[Bmim]HSO_4	71	8	67	(Peleteiro et al., 2016)
	140	20h	-	Xylose	Water/toluene	SBA-15	55	-	-	(Agirrezabal-Telleria et al., 2012)
					Water/DMSO	Amberlyst 70	59			
	140	90 min	-	Xylose	Water/toluene	[Bmim] HSO_4	74	-	-	(Peleteiro et al., 2015)
	140	90 min	-	Xylose	Water/butanone	[Bmim]Cl/$AlCl_3$	75	-	-	(Zhao et al., 2019a)
	140	30 min	-	Arabinose	Water/butanone	[Bmim]HSO_4	60	-	-	(Zhao et al., 2019b)
	170	4h	-	Xylose	Water/toluene	Delaminated H-Nu (Si/Al=29)	47	3	45	(Lima et al., 2008)
	170	30 min	-	Xylose	Water/MIBK	Purolite CT275	72	4	38	(Mittal et al., 2017)
	170	4h	-	Xylose	Water/toluene	[C_3SO_3Hmim]HSO_4	73	6	64	(Matsagar et al., 2015)
	180	30 min	-	Xylose	Water/n-butanol	Cr-deAl-Y	78	5	66	(Wang et al., 2022)
	190	6h	-	Xylose	Water/GVL	SAPO-34	40	-	-	(Bruce et al., 2016)

Table 3. Biphasic solvent system for furfural production from simple sugars and raw biomass (continued)

System	Temp. (°C)	Time		Substrate	Solvent	Catalyst	Yield (%)	Number of runs	*Yield (%)	References
		Residence time	Time on stream							
Continuous	160	8 min	8h	Xylose	Water/MIBK	$AlCl_3$/HCl	90	4**	90	(Guo et al., 2023)
					Water		74	-	-	
	170	396 s	n.p.	Xylose	Water/toluene	H_2SO_4	56	-	-	(Papaioannou et al., 2019)
	225	120 s	n.p.	Xylose	Water/GVL	HCl	90	-	-	(Sener et al., 2018)
	140	13.6 min	24h	Xylose	Water/ dichloroethane	GaUSY-2 with Amberlyst-36	72	-	-	(Aellig et al., 2015)
	180	60 min (LHSV=$1h^{-1}$)	80h	Xylose	Water/1-butanol	Modified hydrated tantalum oxide (TA-p)	56	2**	59	(Li et al., 2015)
	260	3 min	20h	Xylose	Water/toluene	H_3PO_4-Mordenite 13	98	2**	90	(Lessard et al., 2010)
Raw biomass										
Batch	125	126 min	-	Corn stover	Water/DCM	$LiBr.3H_2O$	69	-	-	(Yoo et al., 2017)
				Aspen			84			
	130	30 min	-	Xylan from birch wood	Water/GVL	$Al_2(SO_4)_3$	88	5	73	(Yang et al., 2017)
				Corncob			63	-	-	
	140	1 min	-	Xylan from beech wood	Water/ $[P_{444(14)}]Cl$	HCl	79	3	78	(Morais et al., 2021)
	140	1h	-	Corncob	Water/toluene	$CrCl_3.6H_2O$, NaCl	24	-	-	(Zhang et al., 2014)
	140	1h	-	Xylan	Water/THF	$AlCl_3.6H_2O$/NaCl	64	-	-	(Yang et al., 2012b)
				Corn stover			51			
	140	2h	-	Xylan from corncob	Water/GVL	$LiCl.3H_2O$	77	3	73	(Liu et al., 2021)
	140	3h	-	Xylan	Water/DCM	HCl	76	-	-	(Chheda et al., 2007)

Table 3. Biphasic solvent system for furfural production from simple sugars and raw biomass (continued)

System	Temp. (°C)	Time		Substrate	Solvent	Catalyst	Yield (%)	Number of runs	*Yield (%)	References
		Residence time	Time on stream							
Batch	150	5 min 45 min	-	Bagasse	Water/acetone	H_3PO_4	46	-	-	(Wang et al., 2018)
					Water		39			
	150	120 min	-	Xylan	Water/2-MTHF	$SnCl_4$	78	-	-	(Wang et al., 2015)
Batch	160	60 min	-	Poplar	Water/THF	$AlCl_3.6H_2O$, NaCl	64	-	-	(Yang et al., 2012b)
	160	6h	-	Pine	Water/toluene	H_2SO_4, $ZnSO_4$	64	-	-	(Li et al., 2016)
	160	2h	-	Corn stover	Water/THF	γ-Al_2O_3/SO_4^{2-}	36	-	-	(Yi et al., 2013)
	170	120 min	-	Liquid *Quercus mongolica* hydrolysate	Water/DMSO	H_2SO_4	68	-	-	(Kim et al., 2021)
	170	30 min	-	Cardoon	Water/CPME	H_2SO_4, NaCl	> 80	-	-	(Campos Molina et al., 2012)
	170	50 min	-	Maple wood	Water/MIBK	H_2SO_4	85	-	-	(Zhang et al., 2013)
	170	30 min	-	Corn stover	Water/MIBK	H_2SO_4	80	-	-	(Mittal et al., 2017)
					Water/toluene		76			
	170	100 min	-	Pre-hydrolysis kraft-based dissolving pulp	Water/MIBK	CH_3COOH	60	-	-	(Liu et al., 2013)
					Water		33			
	180	1h	-	Eucalyptus	Water/MIBK	$FeCl_3$	75	-	-	(Zhang et al., 2021)
				Tung shell			99			
	200	2h	-	Pubescens	Water/THF	NaCl	77	-	-	(Luo et al., 2017)
	140	6h	-	Hemicellulose solid	Water/toluene	$[Bmim]HSO_4$	29	-	-	(Peleteiro et al., 2016)

Table 3. Biphasic solvent system for furfural production from simple sugars and raw biomass (continued)

System	**Temp. (°C)**	**Time**		**Substrate**	**Solvent**	**Catalyst**	**Yield (%)**	**Number of runs**	***Yield (%)**	**References**
		Residence time	**Time on stream**							
Batch	170	60 min	-	Concentrated pre-hydrolysis liquor (CPHL)-NaCl	CPHL-NaCl/DCM	Sulfonated carbon based	81	4	25	(Deng et al., 2016)
	170	4h	-	Beechwood	Water/toluene	$[C_3SO_3Hmim]HSO_4$	62	3	57	(Matsagar et al., 2017)
	170	6h	-	Bagasse	Water/p-xylene Water	HUSY (Si/Al=15)	56 18	1	45	(Sahu & Dhepe, 2012)
	190	6h	-	Switchgrass	Water/GVL	SAPO-34	31	3	26	(Bruce et al., 2016)
	190	120 min	-	Bagasse	Water/2-MTHF	$FePO_4$/NaCl	89	5	81	(Wang et al., 2019b)
	190	15 min	-	Corncob	Water/toluene	SO_4^{2-}/SnO_2·MMT	82	5	70	(Qing et al., 2017)
	200	5h	-	Birch wood	Seawater/ THF	Pd-C	41	3	41	(Guo et al., 2018)
Continuous	170	41.7 min (LSHV=1.44 h^{-1})	-	Mixed Northern Hardwood (MNH) chips	Water/THF	HCl	90	-	-	(Xing et al., 2011)
	225	135 s	n.p.	Maple wood	Water/GVL	H_2SO_4	93	-	-	(Sener et al., 2018)

n.p.: not provided
Heterogenous catalyst: White background
Homogenous catalyst: Gray background
*Yield (%): Yield calculated for the last run
**The solid catalyst was regenerated before each run

In biphasic solvent systems, similar trends are observed (Liu et al., 2021; Wang et al., 2022). Beyond affecting reaction rates, temperature also influences the extraction performance of the organic phase. Specifically, the partition coefficient of furfural in the organic phase increases with temperature (Männistö et al., 2017). However, even when furfural is extracted into the organic phase, higher temperatures can still lead to its degradation. To investigate furfural decomposition in biphasic systems, Gómez Millán et al. (2019) conducted auto-catalyzed reactions using CPME and isophorone as extracting solvents at temperatures of 170, 190, and 210 °C with a 1:1 aqueous-to-organic phase volume ratio. Results showed that furfural degradation increased with temperature for both solvents. At 210 °C, the degradation reached 38% with isophorone and below 12% with CPME after 180 min. Additionally, it was observed that furfural degradation increased with reaction time, a topic discussed further in the next section.

4.2.4 Residence time

Residence time/reaction time is another crucial factor that significantly influences the dehydration of xylose (Guenic et al., 2015). Wang et al. (2019a) studied the evolution of furfural yield in a biphasic water/2-MTHF batch system at 190°C, catalyzed by $FePO_4$. Their findings showed that the furfural yield peaked at 88.7% after 120 min but gradually declined to 70% when the residence time was extended to 150 min. They attributed this decline to yield-loss reactions, which were further promoted by both elevated temperatures and prolonged reaction times. Similar observations were reported in a study using ethanol as the extractive phase. In that case, the furfural yield increased significantly during the first 20 min but began to decline when the reaction time was extended to 30 min (Yong et al., 2016). According to liquid–liquid equilibrium principles, furfural in the extractive phase can return to the aqueous phase as degradation of furfural in the aqueous phase progresses. Consequently, prolonged residence time, if excessive, leads to a decline in furfural yields (Yang et al., 2013).

In a continuous production system, the liquid hourly space velocity (LHSV) is a key operating parameter, typically defined as the volumetric flow rate of the feed solution divided by the volume of the loaded heterogeneous catalyst bed or the volume of packing materials (in the case of homogeneous catalyst) in the reactor. In a study on furfural production from waste aqueous hemicellulose solutions catalyzed by H_2SO_4 with tetrahydrofuran (THF) as the extracting solvent, Xing et al. (2011) observed that furfural selectivity initially increased from 76.4% to 87.1% as the LHSV rose from 0.6 h^{-1} to 1.7 h^{-1} at 164°C under a pressure of 800 psig controlled by a back pressure regulator. However, the selectivity declined to 69.6% when the LHSV increased further to 5.61 h^{-1}. Regarding furfural yield, it increased as the space velocity decreased, stabilizing at 77.8% when the LHSV was 1.1 h^{-1}. Similarly, Li et al. (2015) investigated furfural production from xylose in a fixed-bed reactor loaded with 3 mL of a titanium-based catalyst, using a 1-butanol/water biphasic system. By varying the LHSV from 0.25 h^{-1} to 2.0 h^{-1}, they found that at LHSV values below 1.0 h^{-1}, xylose conversion exceeded 90%, and furfural yield exceeded 55%. However, when the LHSV increased from 1.0 h^{-1} to 2.0 h^{-1}, xylose conversion and furfural yield dropped significantly to 60% and 30%, respectively.

These results highlight the trade-offs associated with LHSV. Low LHSV decreases yield and selectivity by increasing residence time, and thus promoting furfural conversion into undesired humins. Conversely, excessive LHSV- shortens the contact time between the pentose and the catalyst, limiting dehydration into furfural and thereby lowering yield. This underscores the importance of optimizing LHSV as a key parameter in continuous processes to enhance furfural yield and selectivity.

4.2.5 Stirring speed

Stirring speed plays a crucial role in furfural extraction efficiency in biphasic batch systems by enhancing the mass transfer rate of furfural from the aqueous phase to the organic phase (Mansur et al., 2003; Cavalcanti et al., 2008). Higher stirring speeds promote the formation of smaller aqueous droplets within the organic phase, increasing the contact area for furfural extraction. This also enhances the mass transfer coefficient of furfural from the aqueous phase to the organic phase. The combined increase in exchange surface area and mass transfer coefficient reduces mass transfer resistance, enabling furfural to transfer more efficiently from the aqueous to the organic phase. Consequently, this improves extraction efficiency and leads to higher furfural selectivity (Jiang et al., 2014).

Conversely, low stirring velocity hinders the interaction between aqueous and organic phases, as larger aqueous droplets form, reducing the exchange surface area. Additionally, under these conditions, the rate of furfural formation exceeds its mass transfer rate to the organic phase (Jiang et al., 2014). Consequently, some furfural remains in the aqueous phase, increasing the likelihood of degradation into undesired humins and ultimately lowering the furfural yield (Yang et al., 2013). This phenomenon was illustrated by Ma et al. (2014), who studied the effect of stirring speed on extraction efficiency and furfural recovery in a pentose-to-furfural reaction catalyzed by $FeCl_3 \cdot 6H_2O$ in a 2-sec-butylphenol/water biphasic system. The results showed that furfural yield increased with stirring speed, reaching a maximum of 81% at 300 rpm. However, further increases in stirring speed led to a slight decline in yield. This decline occurred because rapid stirring induced vigorous fluid rotation, which disrupted the coalescence of the two phases. As a result, the extraction efficiency decreased, negatively affecting both furfural yield and selectivity.

4.3 Comparison of furfural production in biphasic and monophasic solvents in batch systems

As previously mentioned, using simultaneous extraction with an organic solvent in a biphasic system can reduce side-loss reactions and prevent humins formation. Sahu and Dhepe (2012) reported that biphasic conditions yield significantly more furfural compared to a monophasic batch system. For instance, when bagasse was converted using HUSY (Si/Al = 15) as a catalyst, a comparable furfural yield of approximately 55% was achieved in a biphasic system with toluene, MIBK, or p-xylene as extracting solvents at 170°C over 6 h, compared to just 18% in a water-only system. Similarly, Campos Molina et al. (2012) found that a CPME-based biphasic solvent system produced a 40% furfural yield in the acid-catalyzed dehydration of xylose with H_2SO_4, compared to only 28% in a system without CPME. Zhang et al. (2013) investigated the conversion of hemicellulose (mainly xylan) from maple wood, catalyzed by H_2SO_4 in an MIBK-water biphasic system, and achieved a maximum furfural yield of 58.3% at 170°C for 30 min with an aqueous-to-MIBK mass ratio of 1. In contrast, a monophasic system under identical conditions yielded only 9.6%. Using the same organic solvent (MIBK), Li et al. (2014) reported a 60.6% furfural yield from xylose in a water/MIBK system with a solid acid catalyst ($SO_4^{2-}/TiO_2\text{-}ZrO_2/La^{3+}$), compared to a 46.1% yield in a pure water system under the same conditions. These findings underscore that incorporating an organic solvent in a biphasic system can significantly increase furfural yields by limiting side reactions.

4.4 Integration of biphasic solvent systems in continuous furfural production

The use of biphasic solvent systems to enhance furfural production with various catalysts has been primarily studied in batch systems. However, there have been a few investigations on furfural extraction by organic solvents in continuous production systems, as shown in Table 3. This section reviews all available studies on furfural production with simultaneous extraction by organic solvents in biphasic continuous systems.

In 2010, Lessard et al. (2010) reported a high-yield, high-selectivity conversion of xylose to furfural using a protonated mordenite-type zeolite catalyst in a biphasic solution (aqueous and toluene) plug-flow reactor. In this study, a protonated zeolite solid catalyst was dispersed in a xylose solution and thoroughly mixed with the organic solvent at the reactor inlet. The highest furfural yield achieved was 98%, with a selectivity of 98%, at 260°C and 55 atm over a reaction time of 3 min, using toluene as the extracting solvent. However, the authors noted a decline in catalyst activity; after a second pass, the furfural yield dropped from 98% to 90%, despite attempts to regenerate the catalyst through wet oxidation.

In addition to achieving high furfural production with both homogeneous and heterogeneous catalysts in plug-flow reactors, these setups require large quantities of catalyst to be mixed with the xylose solution during conversion. This can lead to substantial acid waste, making the process less environmentally friendly and economical. To address this issue, a fixed-bed reactor offers a promising solution, as demonstrated in Li et al. (2015). This study examined the efficiency of xylose conversion to furfural in a biphasic solution system using a tantalum-based catalyst in a fixed-bed reactor. The highest furfural yield achieved was 59% at a xylose conversion rate of 96%, using 1-butanol as the solvent at 180°C and a LHSV of 1 h^{-1}. After 80 h of continuous operation, the xylose conversion remained stable (over 95%), while the furfural yield showed only a slight fluctuation (from 55% to 59%), indicating excellent stability of the TA-p catalyst in the continuous reaction system. Furthermore, the furfural yield obtained in this continuous system was higher than that achieved in a batch system (45% at 180°C over 3 h), highlighting the advantages of the continuous process.

In the same year, Aellig et al. (2015) explored the potential of fixed-bed reactors by combining a biphasic solvent system with a heterogeneous catalyst for furfural production from xylose and xylan derived from beech wood. Using a mixture of GaUSY-2 and Amberlyst-36 catalysts in a dichloroethane-water biphasic system with an organic-to-aqueous volume ratio of 4:1, the study achieved maximum furfural yields of 72% from xylose and 69% from xylan at 140°C over a reaction time of 3.4 min. These findings underscore the promise of integrated catalyst and reactor design strategies for enhancing furfural production from raw biomass.

Limited studies have been reported on the application of micro/milli-scale reactors for furfural production. In the study of Papaioannou et al. (2019), a milli-reactor operating under the Taylor flow regime was used for the production and in situ extraction of furfural, with diluted H_2SO_4 as the catalyst and toluene as the extraction medium (Figure 6). Inside the reactor, a stainless-steel mesh jacket provided the necessary structural integrity between the aqueous and organic phases. In this setup, the xylose solution, H_2SO_4 solution, and organic solvent were fed separately into the reactor. Due to the enhanced mass transfer properties of the milli-reactor and its precise control of residence time, a high furfural selectivity (70%) at high xylose conversion (80%) was achieved with extremely short residence times (under 2.5 min) at 170°C, using a volume ratio of 2:1 for the organic to aqueous phases.

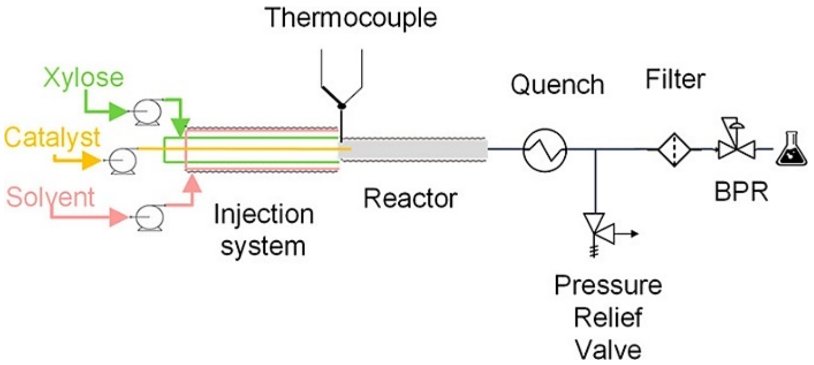


Figure 6. Set-up of continuous reactive extraction system for furfural production (Adapted under the CC-BY-NC-ND license. Copyright 2019 American Chemical Society.)

5. BIPHASIC SOLVENT SYSTEM FOR IMPROVED CATALYST REUSABILITY

In addition to improving furfural yield and selectivity by extracting the produced furfural from the aqueous phase into the organic phase, the use of a biphasic solvent system also enhances catalyst reusability, aligning with sustainable development principles (Magalhães et al., 2021). Catalysts used for furfural production can be broadly classified into two groups based on their physical properties: homogeneous and heterogeneous catalysts. This section explores the use of both catalyst types within biphasic solvent systems, highlighting their advantages, limitations, and the impact of biphasic systems on catalyst performance and reusability.

5.1 The use of homogeneous catalyst in biphasic solvent system

Since homogeneous catalysts remain in the aqueous phase, this phase, containing the catalyst, can be reused once the organic phase has been removed. Guenic et al. (2015) investigated the dehydration of xylose into furfural catalyzed by $FeCl_3$ with NaCl as an additive in a water-CPME biphasic batch system under microwave irradiation. After each catalytic run, the organic CPME phase was removed, and fresh xylose and CPME were added to the recycled aqueous phase containing $FeCl_3$ and NaCl, without introducing additional catalyst. The catalytic activity of $FeCl_3$ was maintained over four consecutive cycles, yielding 76–80% furfural. Besides acting as a catalyst, $FeCl_3$, in combination with NaCl, enhanced furfural separation through the salting-out effect, resulting in improved furfural yields. This finding aligns with the results reported by Wang et al. (2019a), who studied furfural production from bagasse using $FePO_4$ as a catalyst in a water-2-MTHF biphasic system. The study demonstrated that at a NaCl concentration of 800 mg/mL, the furfural yield in the organic phase reached 62.1%, significantly surpassing the 42.7% yield observed in the system without NaCl. By investigating intermolecular weak interactions, Cai et al. (2023) proposed a mechanism for furfural extraction using organic solvents in a biphasic system mixed with metal salts. This mechanism suggests that the addition of metal salts modifies the spatial distribution of weak intermolecular interactions within the solvent system. Consequently, the hydration of water molecules around the solutes is affected, causing changes in distribution coefficients and ultimately facilitating the furfural extraction in the biphasic system.

Later, Delbecq et al. (2016) achieved furfural yields of 76% from xylan and 80% from xylose using a mixture of betaine and formic acid in a CPME-water biphasic batch system under microwave irradiation. Since the produced furfural was extracted into the CPME, the aqueous layer containing the catalyst could be recovered and reused for at least five cycles without a significant drop in furfural yield. However, starting from the fifth cycle, the furfural yield began to decrease, reaching only 75%. This decline was due to the gradual loss of formic acid into the CPME phase, as CPME's water solubility is not zero (11 g/L at 20°C). Indeed, the pH of the aqueous phase shifted from 2.08 to 2.75. However, the aqueous phase remained sufficiently acidic to continue furfural production. A similar observation was made by Wang et al. (2015), who studied the direct conversion of xylose to furfural using $SnCl_4$ as a catalyst in a water-2-MTHF biphasic batch system. The results showed that furfural yield gradually decreased with increasing cycle times. This decrease in catalytic performance was attributed to the loss of $SnCl_4$ from the aqueous phase, as a portion of the water containing $SnCl_4$ was soluble in the organic phase (4.4% w/w at 20°C), reducing the amount of $SnCl_4$ available in the aqueous phase for subsequent reactions. To counter this issue, the use of heterogeneous catalysts, which consistently remain in the aqueous phase, appears to be a more sustainable solution.

5.2 The use of heterogeneous catalyst in biphasic solvent system

In 2016, Deng et al. (2016) developed an efficient method to produce furfural from the pre-hydrolysis liquor of corncob (CPHL) using a biochar catalyst (sulfonated carbon-based catalyst, SCC) as a solid acid catalyst in a water-dichloromethane (DCM) biphasic system. A maximum furfural yield of 81.14% was achieved using this biochar catalyst in the CPHL-NaCl/DCM biphasic system at 170°C for 60 min. The reusability of the biochar catalyst was tested by regenerating it with 98% H_2SO_4 at 150°C for 15 h in an oxygen-free hydrothermal reactor. After five runs, the furfural yield dropped by 16%. With regeneration, the total acidity density slightly decreased over five runs, from 2.97 mmol/g to 2.59 mmol/g. However, the intensity of the adsorption bands corresponding to the S=O stretching modes of $-SO_3H$ in the FTIR spectrum of the fourth regenerated SCC remained comparable to that of the fresh catalyst. Similarly, Qing et al. (2017) investigated the recyclability of a SO_4^{2-}/SnO_2-montmorillonite (MMT) solid catalyst for furfural production from pre-hydrolyzed corncob liquor in a biphasic system using toluene as the extracting solvent. After five runs, the furfural yield decreased from 81.74% to 69.46%, with the catalyst washed only with water and ethanol after each cycle. Elemental and surface area analysis using ICP and BET methods on five-time used catalysts revealed that the recycled SCA exhibited a reduced surface area, decreased pore volume, and a slight reduction in Sn ions bonded to the solid catalyst. These factors, along with the leaching of Sn ions, likely contributed to the decline in the catalyst's performance.

Mittal et al. (2017) observed a similar trend in furfural yield when reusing Purolite CT275 for furfural production from corn stover hydrolysate in an MIBK-water biphasic system. After each catalytic run, both xylose conversion and furfural yield gradually declined, with xylose conversion dropping to 33.4% and furfural yield to 38% by the fourth dehydration reaction. In comparison, the first run achieved a xylose conversion of 69.1% and a furfural yield of 71.5%. The authors attributed this decline to the strong adsorption of reaction products on the active sites of the catalyst. Recently, Wang et al. (2022) reported a furfural yield of 66.1% after five successive runs using a Cr-deAl-Y catalyst, compared to the maximum yield of 77.5% achieved with fresh Cr-deAl-Y catalyst at 180°C for 30 min in an n-butanol/water system. This reduction in yield may be attributed to a decrease in the catalyst's average pore size and specific surface area. However, the surface structure showed no significant changes when comparing the catalyst morphologies before and after the reaction, which could explain the stable catalytic performance.

These findings suggest that while heterogeneous catalysts offer advantages such as easier recovery and reduced mass loss compared to homogeneous catalysts-factors that can influence xylose conversion-they are still susceptible to active site deactivation. Furthermore, the regeneration of heterogeneous catalysts is often necessary before reuse, which adds complexity to the process. This regeneration typically requires additional chemicals and specialized equipment, thereby increasing operational costs.

6. ECONOMIC ANALYSIS OF FURFURAL PRODUCTION IN BIPHASIC SOLVENT SYSTEM

Previous sections have demonstrated that furfural production with simultaneous extraction using an organic solvent in a biphasic system is advantageous, particularly in terms of furfural yield and selectivity. However, scaling this extraction system to larger, industrial applications requires further investigation into its economic feasibility. To address this, several research studies have conducted techno-economic analyses of furfural production in biphasic systems. This section reviews these assessments, focusing on key economic indicators such as capital cost, operational cost, minimum selling price (MSP), and payback period. The summarized results are presented in Table 4.

Xing et al. (2011) conducted an economic analysis of a novel process for producing furfural, along with co-products formic acid and acetic acid, from waste aqueous hemicellulose solutions using a continuous two-zone biphasic reactor. The analysis revealed that furfural could be produced at a cost of $366 per metric ton, which is just 25% of its selling price in the U.S. market in 2011. This estimate assumes a plant capacity of 78 kilotons per year for furfural, 12 kilotons per year for formic acid, and 44 kilotons per year for acetic acid. The total capital cost was reported at 49.5 million $ with the annual operational cost of $24.6 million. Raw materials and utilities were identified as the major cost drivers, comprising 46% of the total production cost. Among the raw materials-dry xylose, NaCl, HCl, and THF-the costs of HCl and THF made up 53.9% of the total raw material expenses. Regarding the installed equipment and associated utility costs, the THF column emerged as the most significant contributor to the fixed capital investment (FCI), accounting for 24.1% of the FCI. The study also suggested opportunities for cost reduction. Using a heterogeneous solid acid catalyst instead of HCl and improving the recovery efficiency of THF-or replacing it with a cheaper organic solvent without compromising performance-could significantly lower the production costs.

Table 4. Techno-economic analyses of furfural production from biomass residues using a biphasic solvent system.

Reference	Xing et al., 2011	Gómez Millán et al., 2021	Zang et al., 2020
Reference year	2011	2021	2020
Feedstock	Mixed Northern Hardwood (MNH) chips	Birch hydrolysate liquor	Switchgrass
Process	Furfural production with the co-products of formic and acetic acids using a continuous two-zone biphasic reactor (water/THF).	Furfural production under auto-catalyzed conditions using a batch reactor in a biphasic system (water/2-sec-butylphenol).	One-pot biomass fractionation and furfural production using aqueous ChCl and MIBK
Product capacity	Furfural: 78 kiloton/year Formic acid: 12 kiloton/year Acetic acid: 44 kiloton/year	Furfural: 5 kiloton/year	Ethanol: 136.2 kiloton/year Furfural: 119.4 kiloton/year Lignin: 106.0 kiloton/year
Total capital cost (Million $)	49.5	12.8	445.4
Annual operational cost (Million $)	24.6	6.6	168.6
Unit production cost	Furfural: $366/t	n.p.	n.p.
Minimum attractive rate of return (MARR) (%)	n.p.	10	10
Minimum selling price	n.p.	Furfural: $1,780/ton	Furfural: $625/ton
Payback period	n.p.	8.9 years	n.p.

n.p.: not provided

[a] The minimum furfural selling price is calculated at NPV equal to zero with MARR of 10%. (with a conversion rate of 1$ = 0.91362€ on September 30, 2019)

[b] Reported as the minimum furfural selling price for MARR of 10%, ethanol selling price of $ 2.55/gal, and lignin selling price of $ 500/ton.

Zang et al. (2020) assessed the techno-economic feasibility of a novel one-pot process for furfural production with the co-production of lignin and ethanol from lignocellulosic biomass. This process is based on one-pot biomass fractionation and furfural production in a biphasic solvent system consisting of aqueous choline chloride (ChCl) and MIBK as the organic phase for in situ furfural extraction. The plant's annual production capacities were substantial: 136.2 kilotons for ethanol, 119.4 kilotons for furfural, and 106.0 kilotons for lignin. The capital investment was significantly higher, at $445.4 million, with an annual operational cost of $168.6 million. The economic analysis revealed that biomass fractionation and cellulose conversion required the largest capital investments, primarily due to the high installation costs associated with pretreatment and distillation equipment. In terms of variable operating costs, feedstock accounted for 40.6% of the total, while other raw material costs in the biomass fractionation area contributed 37.1%. Interestingly, the biphasic solvent system, comprising aqueous ChCl/MIBK, costs approximately $1000 per ton. This relatively high solvent cost reduces the proportion of feedstock costs in the total variable operating cost compared to ethanol production using leading pretreatment technologies such as dilute acid or AFEX (Davis et al., 2013). In the base case study, MSP was estimated at $625 per ton, indicating that the new system could reduce the production price by 37.5%. Even with low selling prices for ethanol and lignin, the proposed co-production system can still produce furfural at a price comparable to its market value (approximately $1,000 per ton) (Alonso et al., 2017). The sensitivity analysis revealed that feedstock price has the greatest impact on the MSP, followed by the cost of ChCl. This highlights the need for future research to focus on reducing ChCl consumption through the use of cheaper solvents, increasing the solid loading during pretreatment, and improving the ChCl recycling ratio. Additionally, sensitivity analysis showed that reaction temperature and solid loading significantly influence the MSP, suggesting that these parameters should be prioritized in future process optimizations.

Gómez Millán et al. (2021) conducted a techno-economic analysis (TEA) for furfural production under auto-catalyzed conditions using xylose and birch hydrolysate liquor in a batch reactor within a biphasic system. The analysis estimated the total investment cost for a plant with a production capacity of 5 kilotons per year to be $15.46 million (with a conversion rate of 1$ = 0.91362 € on September 30, 2019). The total capital cost was estimated at $12.8 million, and the annual operational cost at $6.6 million. Reactor units were identified as the most expensive component, comprising 46% of the total direct cost (TDC), followed by heat exchangers and the distillation column, which contributed 24% and 15% of the TDC, respectively. The minimum selling price (MSP) of furfural was calculated assuming a net present value (NPV) of zero with a discount rate of 10%, resulting in an MSP of $1.78/kg and a payback period of 8.9 years. The authors noted that by increasing the selling price to $2.12/kg, the payback period could be reduced to approximately 5 years. A sensitivity analysis was also performed to assess the impact of various economic factors on the MSP. The analysis revealed that annual operating costs, the discount rate, and total investment had the greatest influence on the MSP. For instance, a 20% increase in operating costs and fixed capital investment led to increases of 11.1% and 4.2% in the MSP, respectively. In contrast, variations in the taxation rate and project lifetime had comparatively smaller effects on the MSP. While the MSP reported by Gómez Millán et al. (2021) was comparatively higher than those of other biphasic solvent systems (Xing et al., 2011; Zang et al., 2020), the authors noted that it was in close alignment with prices reported in the literature and the current market price of petrochemically derived furfural.

In contrast to many earlier reviews, this work highlights in greater detail the capital expenditures including costs for reactors, distillation units, and solvent recovery systems and the operational expenditures such as raw materials, energy, and catalyst use. This distinction is critical for understanding the economic barriers and optimization opportunities in biphasic solvent systems.

Numerous strategies to improve the economic feasibility of industrial-scale furfural production in biphasic systems have been highlighted in this section. Utilizing green and cost-effective chemicals, including organic solvents and catalysts, along with less intensive production technologies, can reduce the need for expensive materials and improve economic viability. Co-producing furfural alongside other valuable chemicals such as ethanol, lignin, acetic acid, and formic acid can further maximize the utilization of lignocellulosic biomass residues and enhance overall profitability. Moreover, optimizing operating parameters, particularly reaction temperature, is crucial for improving the economic performance of furfural production.

7. CHALLENGES AND FUTURE DIRECTION FOR SCALING UP THE BIPHASIC SOLVENT SYSTEMS IN FURFURAL PRODUCTION

The biphasic solvent system has emerged as a promising extraction method to minimize furfural degradation caused by side reactions in the aqueous reaction medium. This approach involves promptly extracting the produced furfural from the aqueous phase into the organic phase, leveraging the high affinity of organic solvents for furfural. The application of biphasic solvent systems to enhance furfural production has been widely investigated, as highlighted in previous sections. One of the major challenges of this method is selecting an appropriate extracting solvent. The solvent must not only be environmentally friendly to meet the principles of green chemistry, i.e., low toxicity, low volatility, and high biodegradability but also exhibit low hydro-solubility to prevent the loss of solvent into the aqueous phase. Solvents classified as VOCs can contribute to air pollution and raise worker safety concerns during large-scale implementation, making solvent selection a critical factor in both environmental sustainability and process economics. Additionally, solvent recyclability must be considered to minimize waste generation and reduce life-cycle emissions associated with continuous operation.

Besides solvent selection, operating parameters such as reaction time and temperature must also be optimized, as furfural degradation intensifies with increased temperature and prolonged reaction time. This was observed by Gómez Millán et al. (2019), who studied furfural decomposition in a biphasic system using isophorone and CPME as extracting solvents at a 1:1 aqueous-to-organic phase ratio. Additionally, once furfural is extracted into the organic phase, it should be promptly removed from the reaction medium and transferred to a lower-temperature zone. This step is crucial, as furfural remains susceptible to decomposition even within the organic phase at elevated temperatures.

The addition of metal salts has been shown to enhance the extraction of furfural from the aqueous phase into the organic phase, due to the salting-out effect, as reported in several studies (Rong et al., 2012; Guenic et al., 2015; Wang et al., 2019a). Additionally, metal salts promote the formation of a biphasic system by increasing the dissociation of water from the water-miscible solvent, thereby improving extraction efficiency (Cai et al., 2023). While this approach yields high furfural recovery, it may present economic challenges due to the additional downstream processing required to recover the salt after production. This issue could potentially be addressed by developing efficient methods to recycle the salt-containing aqueous phase, similar to the reuse of homogeneous catalysts in biphasic systems.

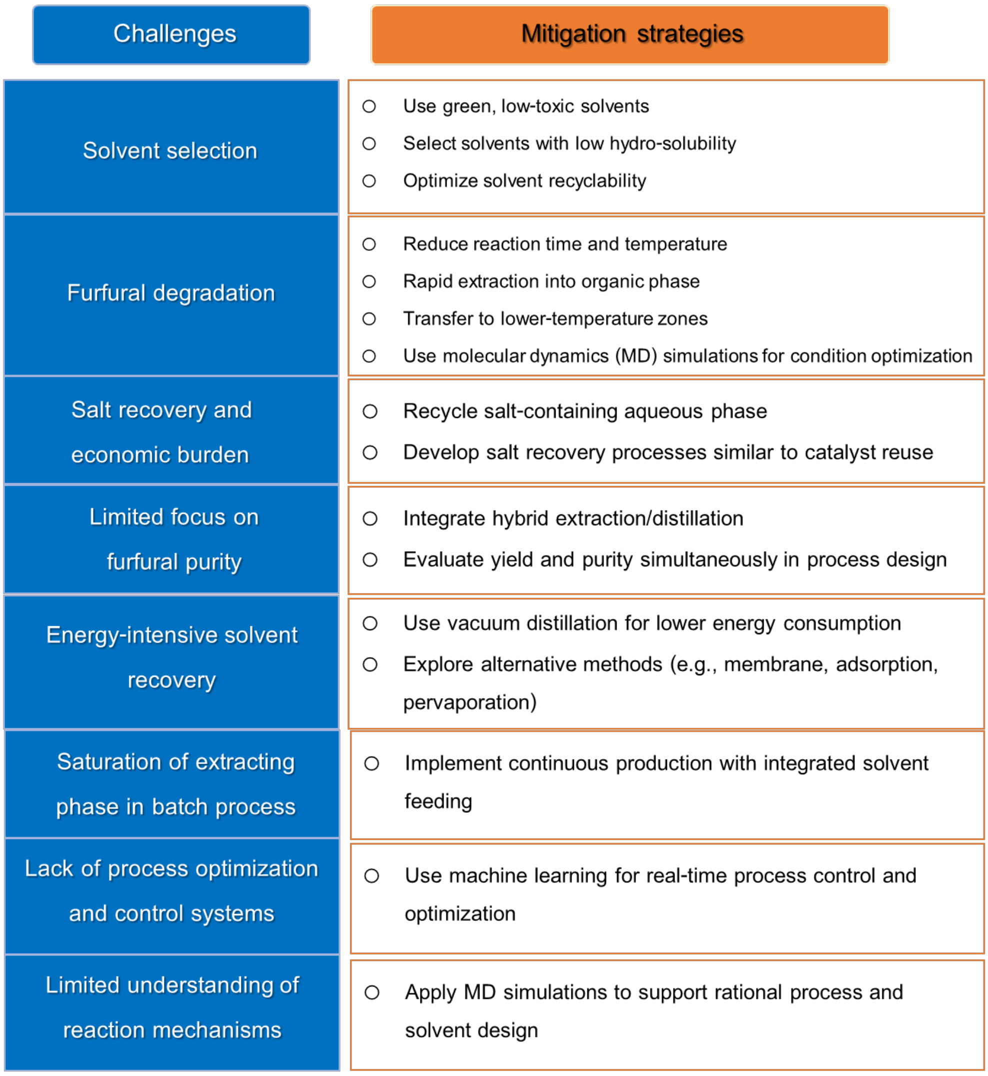
Regarding furfural recovery, relatively few studies have investigated the process up to the recovery of pure furfural. Most research focuses on optimizing the production process to achieve high furfural yields, with limited attention to its purity. However, for industrial applicability, achieving high-purity furfural is equally important, as impurities can compromise product quality and limit end use markets. The lack of standardized reporting on furfural purity across studies also hampers meaningful comparisons and technology transfer from lab to industry. Thus, future work should emphasize not only yield improvements but also detailed analysis of furfural purity, recovery efficiency, and downstream separation feasibility. Some studies have explored the complete process, from production to the recovery of pure furfural, but these have primarily been conducted through simulations. For example, Nhien et al. (2021) proposed a hybrid extraction and distillation process. The simulation results demonstrated that a high furfural purity of 99% could be achieved while reducing reboiler energy consumption by 51.7% and 62% compared to the conventional process, using toluene and butyl chloride as extracting solvents, respectively. Therefore, further research is needed to address furfural recovery, focusing on both yield and purity during the downstream steps. Such advancements are essential to enable the industrial-scale production of furfural.

Among various separation techniques, distillation remains the only method currently used for furfural separation from the end mixture (Mao et al., 2021). In the context of biphasic solvent systems, the boiling point of the solvent plays a critical role in separation efficiency and distillability (Bhaumik & Dhepe, 2016; Zuo et al., 2017). Low-boiling solvents can help prevent furfural degradation during distillation; however, their use often leads to energy-intensive downstream operations due to the large solvent volumes that need to be removed. Conversely, high-boiling organic solvents can reduce energy consumption in downstream processes, as only a small amount of furfural needs to be evaporated. Nonetheless, the thermal instability of furfural at elevated temperatures makes high-boiling solvents less suitable for maintaining optimal process efficiency and product quality.

To align the process with sustainable development principles, solvent recycling is crucial for minimizing solvent usage and reducing the environmental impact associated with solvent waste disposal (Romo et al., 2018). Currently, distillation is the only method used for recovering organic solvents, as it is also the sole means of obtaining pure furfural from the organic phase. For instance, Liu et al. (2021) demonstrated the recycling of GVL by separating it from furfural through facile vacuum distillation after filtration to remove humins. Alternative separation methods such as membrane separation, pervaporation, or adsorption have not yet been investigated for separating furfural and organic solvents. Developing separation techniques that rely on parameters other than boiling points could provide significant benefits, addressing the limitations of solvent selection and offering additional options for recycling furfural and organic solvents in biphasic solvent systems.

The batch process is the most extensively studied method for furfural production in biphasic solvent systems. However, this approach often results in the saturation of furfural within the extracting phase, limiting efficiency. Implementing a continuous feeding system for the extracting solvent in a continuous process could significantly enhance extraction efficiency and unlock greater potential for industrial-scale applications. Moreover, molecular dynamics (MD) simulations offer valuable insights at the microscopic level into the transformation of sugars into furfural and its subsequent extraction within a biphasic system, paving the way for more effective production strategies. Additionally, the integration of machine learning techniques could revolutionize process design and optimization by maintaining optimal solvent conditions, enabling more efficient and consistent extraction, and ultimately improving furfural productivity.

This review highlights the need to shift from yield-centric studies toward a more holistic evaluation of furfural production—one that includes purity benchmarks, solvent recovery methods, and life-cycle environmental impacts. These factors are critical for developing economically viable and environmentally responsible biphasic systems for industrial furfural production. A schematic overview of the major technical, environmental, and economic challenges in biphasic furfural production, along with recommended mitigation strategies, is presented in Figure 7 to illustrate the contributions of this review and guide future research directions.



Challenges	Mitigation strategies
Solvent selection	○ Use green, low-toxic solvents ○ Select solvents with low hydro-solubility ○ Optimize solvent recyclability
Furfural degradation	○ Reduce reaction time and temperature ○ Rapid extraction into organic phase ○ Transfer to lower-temperature zones ○ Use molecular dynamics (MD) simulations for condition optimization
Salt recovery and economic burden	○ Recycle salt-containing aqueous phase ○ Develop salt recovery processes similar to catalyst reuse
Limited focus on furfural purity	○ Integrate hybrid extraction/distillation ○ Evaluate yield and purity simultaneously in process design
Energy-intensive solvent recovery	○ Use vacuum distillation for lower energy consumption ○ Explore alternative methods (e.g., membrane, adsorption, pervaporation)
Saturation of extracting phase in batch process	○ Implement continuous production with integrated solvent feeding
Lack of process optimization and control systems	○ Use machine learning for real-time process control and optimization
Limited understanding of reaction mechanisms	○ Apply MD simulations to support rational process and solvent design

Figure 7. Challenges and mitigation strategies in biphasic furfural production

8. CONCLUSION

This review provides a comprehensive overview of recent advances in biomass conversion to furfural using biphasic solvent systems. Extensive research has explored both homogeneous and heterogeneous catalysts within these systems. By minimizing side reactions that reduce furfural yield and selectivity, biphasic solvent systems not only improve product quality but also facilitate the reuse of the aqueous phase containing catalysts, simplifying product separation. This approach significantly enhances process economics while aligning with sustainable development principles. Optimizing operating parameters such as solvent type and the volume ratio between aqueous and organic phases is essential for achieving high furfural yields. Currently, most furfural production in biphasic systems occurs in batch setups, which often suffer from low biomass conversion rates and high energy demands. To address these limitations, continuous reaction processes with catalyst recycling have been developed, though they remain primarily at the laboratory scale and require further investigation. Notably, the purity of furfural produced in such systems has not yet been verified, and advancements in the recovery and separation of pure furfural from the reaction medium are still necessary. The economic analysis indicated that furfural production from raw biomass in a biphasic system is cost-effective, primarily due to its lower pretreatment costs compared to other methods. Additionally, the co-production of furfural with other valuable products further enhanced the economic feasibility of the process. Scaling up and refining catalytic biphasic solvent systems that minimize catalyst loss and enable effective recycling, as well as developing effective methods for recovering pure furfural remain key challenges for future research and industrial application.

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