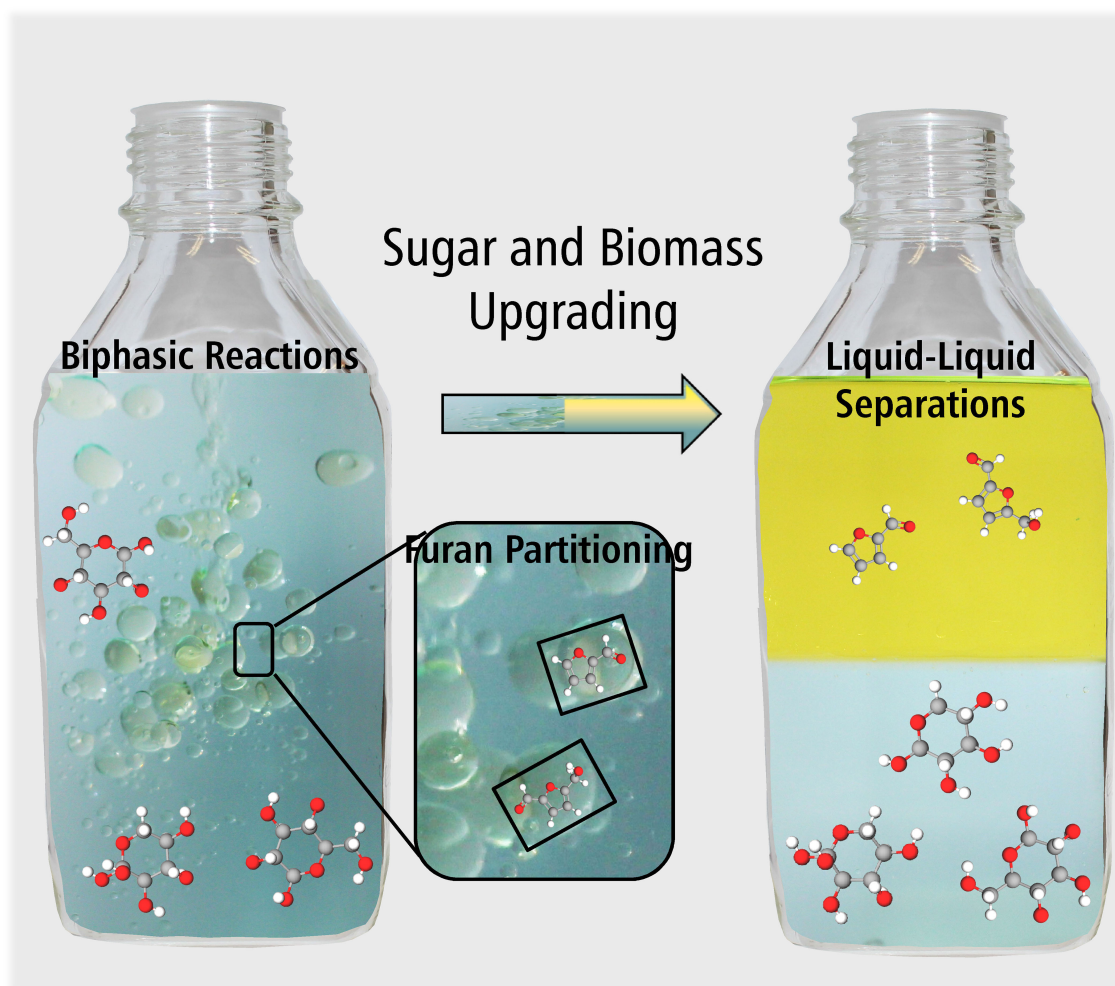


# Conversion of Sugars and Biomass to Furans Using Heterogeneous Catalysts in Biphasic Solvent Systems

Joelle E. Romo,<sup>[a]</sup> Nathan V. Bollar,<sup>[a]</sup> Coy J. Zimmermann,<sup>[a]</sup> and Stephanie G. Wettstein<sup>\*[a]</sup>



Within the last decade, interest in using biphasic systems for producing furans from biomass has grown significantly. Biphasic systems continuously extract furans into the organic phase, which prevents degradation reactions and potentially allows for easier separations of the products. Several heterogeneous catalyst types, including zeolites, ion exchange resins, niobium-based, and others, have been used with various organic solvents to increase furan yields from sugar dehydration

reactions. In this minireview, we summarized the use of heterogeneous catalysts in biphasic systems for furfural and 5-hydroxymethylfurfural production from the past five years, highlighting trends in chemical and physical properties that effect catalytic activity. Additionally, the selection of an organic solvent for a biphasic system is extremely important and we review and discuss properties of the most commonly used organic solvents.

## 1. Introduction

Biphasic reaction systems present a viable route to platform chemicals, such as furfural and 5-hydroxymethylfurfural (HMF), from lignocellulosic biomass. These systems take advantage of the differences in hydrophobicity of reactants and products and typically lead to higher product yields than with monophasic, aqueous systems. In the case of biomass reactions, products that might degrade in the aqueous layer, such as furans, partition to the organic layer while the sugar and acids remain in the aqueous layer. Therefore, better downstream separations occur and less energy is needed for recycling solvents since the products are concentrated in the organic phase. Additionally, the solvent properties, such as boiling point, can be selected to improve separations. For example, a higher boiling solvent could be used to obtain desired products from the top of a distillation column or a lower boiling solvent could be used if the product is heat sensitive.

Lignocellulosic biomass is abundant in the form of corn stover, pulp and paper mill waste, food waste, switchgrass, and many other sources.<sup>[1]</sup> Biomass is composed of three main fractions: cellulose, a glucose polymer, hemicellulose, a polymer mainly composed of xylose, and lignin, which is made up of aromatic compounds. Additionally, biomass contains inorganic salts, ash, and proteins, among other components that may affect heterogeneous catalysis.<sup>[2]</sup> Although much progress has been made in upgrading the sugar fractions to fuels and chemicals,<sup>[3]</sup> obtaining high yields of platform chemicals economically remains a challenge. Using biphasic systems for biomass hydrolysis is a potential solution that has many advantages since solvents can prevent furan polymerization,<sup>[4]</sup> concentrate products by using a lower volume of solvent,<sup>[5]</sup> and enhance biomass solubility, which leads to less solids remaining after reaction and potentially faster reactions.<sup>[6]</sup>

An ideal solvent for a biphasic system would be one that has minimal solubility in the carrier (in biomass processing, the

carrier is likely water), a high relative volatility when compared with the solutes for easy recovery, and a high partition coefficient for the solute, which is the amount of solute in the organic phase relative to the amount of solute in the aqueous phase.<sup>[7]</sup> The simplest biphasic system is one that naturally separates and does not require the use of modifiers. Modifiers, such as NaCl, are sometimes used to create biphasic systems when they would not normally exist and/or increase the partition coefficient of the solute. (The increase in the partition coefficient is commonly referred to as the salting-out effect.) However, modifiers may interact with heterogeneous catalysts; for example, ion exchanging with active sites, which adds a layer of complexity to the system. Since modifiers may require an additional separation step to recover and add cost to the process, a biphasic system without modifiers is preferred.

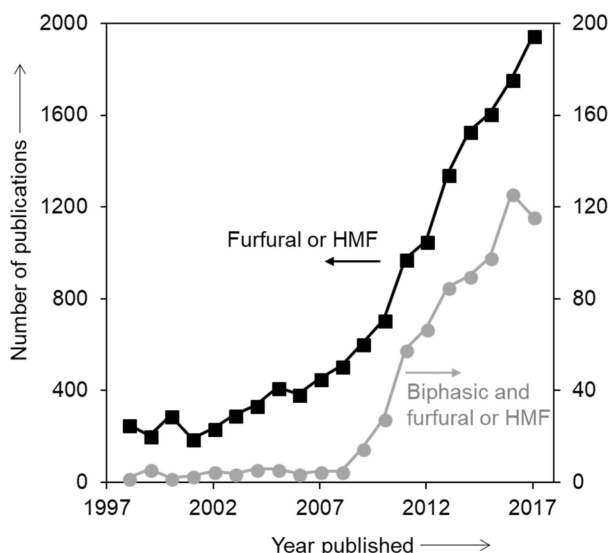
The addition of a solvent will likely require an additional separation step, which adds cost to the process. Due to the elevated price of many organic solvents, the organic layer must be recovered and reused in order for the process to be economically viable.<sup>[8]</sup> If the solvent is soluble in the carrier (and vice versa), additional processing volume and a separation step to recover the carrier may be needed. Other properties, such as viscosity and toxicity, also need to be considered, but perhaps the most important property for catalysis is if the solvent participates in the reaction since that could significantly affect resulting products. For the vast majority of biphasic reactions, an inert solvent is preferred.

One common use of biphasic systems is to produce furans, such as HMF from glucose or fructose and furfural from xylose. The organic solvent extracts the furans and reduces degradation and further reactions. HMF is a building block for many chemical applications including liquid fuels, platform chemicals, polyester building blocks, and others.<sup>[9]</sup> Furfural can also be used as a solvent or upgraded to many chemicals such as furfuryl alcohol, which can then be used to produce furan resin prepolymers, and with further hydrogenation, tetrahydrofurfuryl alcohol, which is used as a solvent in agricultural applications.<sup>[10]</sup>

Publications on furfural, HMF, and biphasic reactions have grown considerably in the last decade (Figure 1). Previous works have reviewed furfural and HMF as value-added products derived from biomass, including discussion of suitable feedstocks, synthesis methods, and pathways for upgrading to fuels.<sup>[5,9a,11]</sup> Reviews by Saha et al.<sup>[9a]</sup> and van Putten et al.<sup>[11b]</sup> provide a thorough review of biphasic systems used for synthesizing HMF with homogeneous and heterogeneous

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**Figure 1.** Number of review or research articles published per year containing “Furfural or HMF” (■) or “Biphasic and furfural” and “Biphasic and HMF” (●) that appeared on a sciencedirect.com search 5/4/18.

catalysts through 2013, while Dutta et al.,<sup>[11a]</sup> Lange et al.,<sup>[5]</sup> and Delbecq et al.<sup>[12]</sup> reviewed multiple upgrading reactions and methods for furfural production. To the best of our knowledge, no reviews thoroughly cover biphasic furan production in publications since 2013.

In this paper, we review publications from the last five years regarding biphasic production of furfural and HMF using heterogeneous catalysts ranging from zeolites to polymers. We discuss the physical and chemical properties of heterogeneous catalysts that contribute to their activity, the use of phase

modifiers to increase partitioning in biphasic systems, considerations of solvent selection, and overall trends in conversion and yields using biphasic reactions.

## 2. Heterogenous Catalysts

Heterogeneous catalysts have been increasingly popular for furan production.<sup>[13]</sup> Unlike homogeneous acid catalysts that can be corrosive and require special handling, heterogeneous catalysts can easily be integrated into reaction systems and are easier to recover. Different classes of heterogeneous catalysts have unique acidities, hydrophobicities, and surface structures that contribute to their activity.<sup>[14]</sup> Included among these are zeolites, polymer-based, niobium-based, clays, and carbon-based catalysts.

### 2.1. Zeolites

Microporous zeolites have been widely used as catalysts for the production of furfural and HMF in biphasic systems due to their chemical resistance, acidic properties, and stability in high temperature environments. A review by Ennaert et al. on using zeolites for biomass conversion contains an excellent background on fundamental zeolite catalysis including the challenges of using zeolites in high temperature, liquid reactions.<sup>[15]</sup>

The zeolite framework can be chosen to select pore size, and the acidity can be tuned by atom composition, including changing the Si/Al ratio. The amount of Al is related to the Brønsted acidity, which, for example, directly contributes to the dehydration of xylose to furfural.<sup>[16]</sup> Table 1 lists some of the



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Stephanie G. Wettstein earned her BSc in Paper Science at the University of Wisconsin – Stevens Point and her PhD at the University of Colorado – Boulder under the supervision of Prof. John Falconer and Prof. Rich Noble. Following, her postdoctoral studies were performed under the guidance of Prof. James A. Dumesic at the University of Wisconsin-Madison studying catalytic lignocellulose conversion and upgrading. Prof. Wettstein continues research in catalysis and separations with the goal of understanding fundamental properties of catalysts to improve production of green chemicals.



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**Table 1.** Properties of zeolites used for furfural production from xylose at 170 °C, unless otherwise noted, in biphasic systems.

Zeolite	Framework	Pore size <sup>[a]</sup> [nm]	Si/Al ratio	Surface area	Total acidity [μmol/g]	Reaction time [h]	Yield	Ref.
H-Y	FAU	0.74	4	617	1384	1	19 <sup>[b]</sup>	[17]
MOR-10	MOR	0.7	10	400	480	6	61	[18]
H-USY	FAU	0.61	15	873	550	6	56	[19]
CHA-20	CHA	0.38	20	548	1030	6	60	[18]
ITQ-2	–	0.7	24	623	198	16	66	[20]
H-MCM-22	MWW	0.55	24	333	204	16	70	[20]
H-MCM-22	MWW	0.55	38	497	168	24	60	[20]
H-MCM-22	MWW	0.55	38	497	168	32	68	[20]

[a] From <http://www.iza-structure.org/databases/>; [b] At 160 °C.

recently used zeolites in biphasic systems and shows the wide range of pore sizes and acidities that have been used for furfural production from xylose in recent years. Antunes et al. used H-MCM-22 zeolite and achieved higher furfural yields (70%) from xylose in a toluene/H<sub>2</sub>O biphasic system (7:3 volume ratio) compared to the pure water system (54%). Decreasing the Si/Al ratio from 38 to 24 increased the acidity of the catalyst from 168 to 204 μmol/g, which increased furfural yields at shorter reaction times (Table 1).<sup>[20]</sup> The catalyst with the lower Si/Al ratio required less reaction time (16 versus 24 h), which represents a higher turn-over frequency, and was recyclable four times with no loss of furfural yield.<sup>[20]</sup> Other researchers used zeolites with Si/Al ratios ranging from 4–20 and higher acid site concentrations, but did not achieve the yields Antunes et al. did with H-MCM-22 (Table 1).

Researchers also used bamboo and bagasse as the xylose source, multiple solvents, and different zeolites with the highest furfural yields around 55% (Table 2). For bagasse, compared to the monophasic, aqueous system, where only 18% furfural was obtained, the biphasic systems led to significantly higher yields and showed that zeolites can be successfully used in biphasic dehydration reactions with biomass.<sup>[19]</sup>

Zeolites have also been explored for converting fructose to HMF in biphasic systems. Similar to work for furfural production from H-USY,<sup>[19]</sup> Pande et al. optimized HMF production in a biphasic MIBK/H<sub>2</sub>O system with modified H-USY zeolites since MIBK resulted in higher HMF yields than toluene, IPA, and ethanol. The polar IPA and ethanol solvents had lower partition coefficients than the nonpolar MIBK and toluene solvents, which are also less miscible in water. HMF yields of 32% and 65% and furfural yields of 31% and 11% (resulting from HMF degradation to formaldehyde) were achieved using commercial H-USY and 10 wt% H<sub>3</sub>PO<sub>4</sub> treated H-USY, respectively.<sup>[21]</sup> The acid treatment decreased the Al content (from 2.8 wt% to 1.2 wt%) of the H-USY and therefore, increased the Si/Al ratio.

The total acidity decreased from 860 μmol/g to 270 μmol/g with the H<sub>3</sub>PO<sub>4</sub> acid treatment, which the authors hypothesized enhanced hydrothermal stability, hydrophobicity, and increased the mesoporosity of the catalyst. H-USY treated with H<sub>2</sub>SO<sub>4</sub> also had lower acidity and Al content, but did not have increased mesoporosity like the H<sub>3</sub>PO<sub>4</sub> treated zeolite. For the H<sub>2</sub>SO<sub>4</sub> treated H-USY, the HMF and furfural yields were equivalent or less than the non-treated H-USY indicating that the increased mesoporosity of the H<sub>3</sub>PO<sub>4</sub> treated H-USY was an important factor to the increased yields.<sup>[21]</sup>

Despite results showing increased activity with lower acidity for furfural production,<sup>[21]</sup> higher catalyst acidity was an important factor to achieve high HMF product yields. Ordonsky et al. tested zeolites, including ZSM-5, BEA, and MOR for HMF production in a MIBK/H<sub>2</sub>O system. MOR had the highest acidity (11.7 Si/Al, 1100 μmol/g) and had the highest HMF selectivity achieving approximately 65% selectivity at 80% conversion (165 °C). Although ZSM-5 had a relatively high acidity (13 Si/Al, 966 μmol/g), its pore size of 0.55 nm<sup>[22]</sup> may have restricted the diffusion of fructose (0.9 nm<sup>[23]</sup>), leading to many of the acid sites not being accessible. Both MOR and BEA have larger pores (0.7 and 0.75 nm,<sup>[22]</sup> respectively), which would reduce mass transfer limitations of fructose<sup>[24]</sup> since it is known that zeolites can adsorb molecules up to 0.1<sup>[25]</sup> to 0.2<sup>[5]</sup> nm larger than the pore diameter. When using microporous catalysts, internal diffusion limitations are an important consideration; however, the lower HMF yields with BEA, despite its larger pore diameter, were attributed to the lower acidity (15.6 Si/Al, 860 μmol/g) compared to MOR.<sup>[24]</sup>

The addition of modifiers to biphasic systems when using zeolite catalysts is uncommon, perhaps due to catalyst deactivation from mineral salts. Biomass impurities, including Na and K, are known to decrease zeolite activity<sup>[12]</sup> and salts can cause the Si and Al sites to leach, which, even though the crystalline structure remains intact, significantly impacts the

**Table 2.** Furfural yields using zeolite catalysts and different biomass sources at 170 °C.

Xylose source	Weight percent	Org:H <sub>2</sub> O ratio	Solvent	Catalyst	Reaction time [h]	Furfural yield [%]	Ref.
Bamboo	3.5	4:1	toluene	CHA-20	10	55	[18]
Bamboo	3.5	4:1	toluene	MOR-10	10	49	[18]
Bagasse	1	1:1	toluene	H-USY	6	54	[19]
Bagasse	1	1:1	MIBK	H-USY	6	55	[19]
Bagasse	1	1:1	p-xylene	H-USY	6	56	[19]
Bagasse	1	–	water	H-USY	6	18	[19]



catalyst acidity.<sup>[26]</sup> However, introducing NaCl in a sec-butylphenol (SBP)/H<sub>2</sub>O biphasic system using ZSM-5 as the catalyst showed increased HMF selectivity from glucose. Unmodified systems without NaCl had low HMF selectivity compared to the modified system, which had 81% HMF selectivity at 100% conversion (170 °C, 30 min). Gardner et al. hypothesized a synergistic effect with the NaCl present in the aqueous phase. The hydrolysis was enhanced by releasing the Al<sup>3+</sup> species from the zeolite, which isomerized the glucose to fructose, in addition to increasing product into the organic phase.<sup>[26]</sup> Although high HMF yields could be obtained from the leached acid sites in the solution,<sup>[26]</sup> recyclability is likely poor and regeneration would be extensive.

The high furan yields resulting from the zeolite catalysts demonstrate the utility of multiple organic solvents as extracting solvents in biphasic systems in addition to the wide variety of zeolites that can be used for platform chemical production. Furan yields benefited from some acidity and the increased mesoporosity created with acid treatments. Additionally, some zeolites may have had internal diffusion limitations, which shows that pore size is an important consideration for catalytic reactions.

## 2.2. Polymers/Ion Exchange Resins

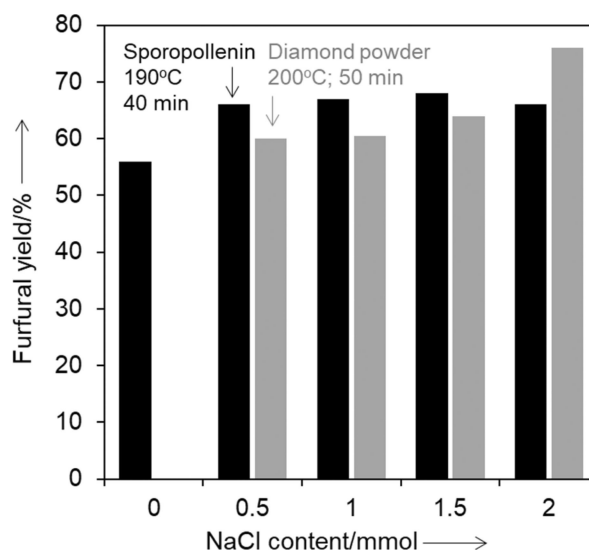
Acidic, ion exchange resins are attractive catalysts with high activity, mechanical stability, and low cost. These resins have tunable properties related to the monomer type, degree of polymerization, and functional groups added to the polymer framework. Additionally, their macroporous structures have high surface area with large pores that can be formed during polymerization.<sup>[27]</sup> The large pores in ion exchange resins allow sugar molecules to easily diffuse into their macropores to access acid sites.<sup>[16]</sup> These polymeric catalysts, typically supplied as spherical pellets, have been shown to have excellent recovery and reusability, but can have performance issues due to leaching of acid sites.<sup>[27]</sup>

Commercially available ion exchange resins, including Amberlyst, Purolite, and Nafion have been used for furan dehydration reactions with varying results. These solid, sulfonated polymers have strong Brønsted acidity, high activity, and hydrophobic structural characteristics.<sup>[14]</sup> Mittal et al. used Purolite CT275 and Nafion NR50 in MIBK biphasic systems to convert pentose-rich corn stover hydrolysate into furfural. Unlike common ion exchange resins, which are only stable to around 150 °C, Purolite and Nafion showed increased thermal stability up to 180 °C and 200 °C, respectively. The highest yields were achieved at an organic to aqueous volume ratio of 2:1 using hydrolysate equivalent to 8 wt% monomeric pentose sugars (170 °C; 20 min). The MIBK/H<sub>2</sub>O biphasic system resulted in high furfural yields for both Purolite (80%) and Nafion (78%) catalysts, but the Nafion system required eight times the catalyst loading (400 mg/g pentose sugar) than the Purolite system. The significantly lower catalyst loading for the Purolite system was attributed to the higher H<sup>+</sup> concentration compared to the Nafion catalyst,<sup>[28]</sup> which despite its high acidic

properties, had a lower surface area (0.02 m<sup>2</sup>/g) that limited its performance.<sup>[16]</sup> The furfural yields from the heterogeneous systems were similar to using 0.05 M H<sub>2</sub>SO<sub>4</sub> indicating that solid-acid catalysts in biphasic systems could be used to replace homogeneous catalysts. However, upon catalyst recycling (no washing or regeneration), the furfural yields decreased significantly with the Purolite catalyst from 71.5% for 1st run to 38.0% for the 4th run, resulting from what the researchers attributed to the blocking of active sites.<sup>[28]</sup>

Despite challenges that arise from Nafion's low surface area, Le Guenic et al. used Nafion NR50 in a cyclopentyl methyl ether (CPME)/H<sub>2</sub>O NaCl modified biphasic system, obtaining maximum furfural yields of 80% (170 °C, 40 min) from xylose under microwave irradiation. Decreasing the NaCl content from 2.5 wt% to 0.25 wt% decreased furfural yields by approximately 12% indicating that the salting-out effect was stronger at higher NaCl concentrations.<sup>[29]</sup> In a similar study, Wang et al. presented an alternative biopolymer, sulfonated sporopollenin, for furfural production due to its high thermal stability and unique hydrophobic cavity within its structure. In a CPME/H<sub>2</sub>O biphasic system modified with NaCl, furfural yields of 69% were achieved (190 °C, 40 min) under microwave irradiation. The catalyst was able to be recycled 10 times with only a 5% decrease in furfural yield with NaCl present and a 10% decrease in furfural yield with no NaCl present.<sup>[30]</sup> As also seen by Le Guenic et al.,<sup>[29]</sup> Wang et al. found that increasing the NaCl content produced higher furfural yields in CPME/H<sub>2</sub>O biphasic systems (3:1 volume ratio; Figure 2). In the modified biphasic system, NaCl interacts with carbocation intermediates in the dehydration reaction in addition to increasing the partitioning of furfural into the organic phase; thus, furfural production is increased compared to aqueous systems.<sup>[30]</sup>

In addition to these benefits, the NaCl modifier was also found to have synergetic effects with the Nafion NR50 catalyst



**Figure 2.** The effect of NaCl content on furfural yields with heterogeneous catalysts in CPME/H<sub>2</sub>O biphasic systems from Wang et al. for dehydration of xylose over sulfonated sporopollenin<sup>[30]</sup> (black bars) and Delbecq et al. for sulfonated diamond powder<sup>[31]</sup> (gray bars).

by Le et al. A cation exchange between the sulfonated polymer catalyst and modifier released HCl which contributed to the dehydration of xylose as a homogeneous catalyst. Further studies on the pH of the Nafion NaCl system compared to homogeneous HCl reactions confirmed that the Nafion NR50 activity contributed to higher furfural yields, but was not a completely heterogeneous reaction.<sup>[29]</sup>

Along with the zeolite catalysts mentioned in the previous section, Ordonsky et al. also used Amberlyst-15 in a biphasic MIBK/H<sub>2</sub>O system to increase selectivity to HMF compared to a monophasic aqueous system. The addition of MIBK as an extracting organic solvent increased HMF selectivity to a maximum of 77% (135 °C, 5:1 ratio MIBK/H<sub>2</sub>O) compared to 66% selectivity with a 1:1 ratio MIBK/H<sub>2</sub>O and 55% selectivity in water all at 35% conversion.<sup>[32]</sup> As seen by Mittal et al. with furfural and Purolite,<sup>[28]</sup> increasing the organic to aqueous ratio increased the HMF selectivity and running the reaction in a biphasic system was found to suppress further HMF conversion.<sup>[32]</sup> MIBK has a high partition coefficient for both furfural (6.4 in 2:1 volume ratio<sup>[28]</sup>) and HMF (2.7 in 3:1 volume ratio<sup>[32]</sup>), which makes it an effective extracting solvent in biphasic systems.

High furfural yields can be achieved using ion exchange resins but leaching of the active sites could result in homogeneous reactions and the inability to recycle the catalyst. Nevertheless, synergistic effects between modifiers and ion exchange resins could increase furan selectivity and yield. Ion exchange resins benefited from increasing the organic to aqueous ratio, increased acidity, and adding a modifier to the system.

### 2.3. Niobium-based

Niobium-based catalysts can be used for dehydration reactions due to their acidic properties, high stability in aqueous reactions, chemical safety, and relatively low cost.<sup>[33]</sup> Niobium-based catalysts have been used as promoters, with supports, and as solid acid catalysts in catalytic reaction systems.

Compared to monophasic systems, using niobium catalysts in biphasic systems increased furfural yields with CPME, toluene, THF, and xylene as organic solvents. Research by Molina et al. showed that biphasic CPME/H<sub>2</sub>O systems increased furfural yields of up to 14% from xylose over aqueous and monophasic GVL/H<sub>2</sub>O systems (130 °C, 6 h) using niobium oxide (Table 3).<sup>[34]</sup> Garcia-Sancho et al. investigated acidic mesoporous

niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>; 198.6 μmol/g) catalysts to convert xylose into furfural in toluene/H<sub>2</sub>O biphasic systems achieving yields of 54% (170 °C; 90 min).<sup>[35]</sup> Further work found that using 12 wt% Nb on a mesoporous silica support (SBA-15) with moderate acidity (318 μmol/g) significantly increased the furfural selectivity. The furfural selectivity was found to be 93% at 85% conversion (160 °C) compared to the monophasic system, which had around 54% furfural selectivity at approximately 84% conversion.<sup>[36]</sup> Similar work using amorphous niobium oxide by Gupta et al. evaluated THF, toluene, and xylene as organic solvents. The biphasic toluene/H<sub>2</sub>O system was found to have the highest selectivity for furfural (72% at greater than 99% conversion) compared to the pure water system (48% furfural selectivity at 93% conversion).<sup>[37]</sup>

Pholjaroen et al. used acidic niobium phosphate (NbP, 402 μmol/g) as the catalyst to convert xylose to furfural in biphasic systems, but achieved lower yields than the other niobium-based catalysts (Table 3).<sup>[17]</sup> As seen with other niobium catalysts,<sup>[37]</sup> in biphasic systems toluene provided the highest furfural yield compared to MIBK, n-butanol, and 2-butanol. The researchers hypothesized that toluene provided higher yields due to its low polarity and higher furfural affinity. Additionally, increasing the organic to aqueous volume ratio increased furfural yield up to a 1.5 toluene/H<sub>2</sub>O ratio.<sup>[17]</sup>

Niobium-based catalysts have also been used for glucose and fructose dehydration to HMF. Yang et al. used hydrated Nb<sub>2</sub>O<sub>5</sub> in a 2-butanol/H<sub>2</sub>O biphasic system resulting in HMF yields of 89% from fructose (50 min) and 54% from glucose (140 min) at 160 °C. Catalysts recycled seven times did not lose activity or stability and reactions with real biomass, hydrolyzed Jerusalem artichoke, yielded 65% HMF (160 °C, 120 min).<sup>[33]</sup>

Peng et al. explored Nb/SBA-15 in biphasic THF/H<sub>2</sub>O systems modified with NaCl for HMF production. In reactions with glucose (165 °C, 3 h) and cellulose (170 °C, 8 h), HMF yields were 62% and 51%, respectively. The Nb/SBA-15 catalyst had minimal loss in activity after 10 cycles with regeneration between each cycle.<sup>[38]</sup>

These results demonstrate the capabilities of niobium type catalysts for furan production with moderate to high yields in biphasic systems using different organic solvents. No researchers reported leaching and, when reported, recyclability was good. Niobium-based catalysts benefited from low polarity solvents and increased organic to aqueous ratios.

### 2.4. Clays

Inexpensive clay minerals as solid acid catalysts have received increased attention due to their tunable acidity and reusability.<sup>[14]</sup>

Nanao et al. used montmorillonite-type clays (JCSS-3101, JCSS-3102, and K10) to convert xylose and bamboo powder into furfural in toluene/H<sub>2</sub>O biphasic systems (4:1 volume ratio). Furfural yields ranged from 31–47% for the three clay types at 140 °C and 0.22 wt% xylose in the biphasic system. With bamboo powder catalyzed by JCSS-3102 and K10 (170 °C; 10 h), furfural yields were 46% and 55%, respectively;<sup>[39]</sup> however, the

**Table 3.** Furfural yields for the biphasic dehydration of xylose over niobium-based catalysts in biphasic systems.

Solvent	Org:Aq ratio [v/v]	Catalyst	Temp [°C]	Time [h]	Xylose [wt%]	Furfural yield [%]	Ref.
CPME	8:3	NbO	130	6	4.5	58	[34]
Toluene	7:3	Nb <sub>2</sub> O <sub>5</sub>	170	1.5	3.2	53.5	[35]
Toluene	3:2	NbO	120	3	1.4	72	[37]
Toluene	5:3	NbP	160	1	4.2	22.5	[17]
Toluene	5:3	NbP	210	1	4.2	42	[17]

xylose loadings were low and higher xylose loadings would likely result in lower yields.

Significant research has been performed on montmorillonite-type (MMT) clays with modifiers in biphasic systems with improved yields. Li et al. investigated a montmorillonite with tin (Sn-MMT) catalyst for the conversion of xylose to furfural in a SBP/H<sub>2</sub>O biphasic system with both DMSO and NaCl as modifiers in the aqueous phase. Addition of the modifiers improved furfural yields (Table 4) and running the reaction as a SBP/H<sub>2</sub>O biphasic system increased furfural yields to a maximum of 77% (180 °C, 0.5 h). Reactions with extracted biomass from corncob instead of xylose resulted in a maximum furfural yield of 54% (180 °C, 2 h), demonstrating the practical applications of Sn-MMT in the modified biphasic system.<sup>[40]</sup> In other research, Lin et al. also used sulfated Sn-MMT as a solid acid catalyst for the conversion of xylose and xylan to furfural in a MTHF/H<sub>2</sub>O biphasic system. Saturating the system with NaCl increased furfural yields from xylose by almost 13% over the aqueous system and had the highest furfural yields of near 80% from xylose (2 h) and 77.3% from xylan (1.5 h) at 160 °C.<sup>[41]</sup> Using the same modified biphasic system (SBP/NaCl-DMSO-H<sub>2</sub>O) with pretreated corncob, a maximum furfural yield of 58% (190 °C; 10 min) was obtained from hemicellulose using Sn-MMT.<sup>[42]</sup> In subsequent work using structural characteristics of alkali-extracted corncob liquid analyzed with NMR, Li et al. hypothesized that polydispersity contributed to increased furfural production. The corncob fractions with the highest polydispersity, HO<sub>30</sub> (6.3) and HF<sub>30</sub> (5.7), had the highest furfural yields compared to fractions with lower polydispersity (< 4).<sup>[43]</sup>

Pretreated corncobs were also used by Qing et al. along with Sn-MMT catalysts, NaCl as a modifier, and solvents including toluene, MIBK, CPME, and GVL. Toluene yielded the most furfural at 82% (190 °C; 15 min) from xylose compared to only 44% in the aqueous system. Using pretreated corncob in the optimized reaction system (1:1 volume ratio, 4 wt% NaCl) led to furfural yields of 66% compared to 44% with no modifier present. Further increasing the reaction time showed decreased furfural yields due to accelerated degradation reactions of furfural.<sup>[44]</sup>

Clay catalysts have been demonstrated effective for furan production with moderate yields from both sugars and biomass. The catalysts benefited from using aqueous phase modifiers as well as increased reaction temperatures.

**Table 4.** Furfural yields for the dehydration of 10 wt% xylose over clay-based catalysts at 150 °C and 3 h unless noted.<sup>[40]</sup>

Solvent	Modifier(s)	Catalyst	Furfural yield [%]
H <sub>2</sub> O	none	–	3.2
H <sub>2</sub> O	DMSO	–	8.7
H <sub>2</sub> O	DMSO	Sn-MMT	27.2
H <sub>2</sub> O	NaCl + DMSO	Sn-MMT	31.8
H <sub>2</sub> O/SBP	DMSO	Sn-MMT	55
H <sub>2</sub> O/SBP	NaCl + DMSO	Sn-MMT	67
H <sub>2</sub> O/SBP <sup>[a]</sup>	NaCl + DMSO	Sn-MMT	76.8

[a] 180 °C and 0.5 h.

## 2.5. Carbon-based Catalysts

Carbon-based heterogeneous catalysts are attractive since they have high BET surface area, good stability, and controllable acidity with modified functional groups.<sup>[14]</sup>

Wang et al. demonstrated the use of a heterogeneous sulfonated carbon-based catalyst for the dehydration of xylose and xylan to furfural in a CPME/H<sub>2</sub>O 3:1 volume ratio biphasic system. Optimization of the reaction system resulted in furfural yields of 60% and 42% from xylose and xylan, respectively (190 °C; 1 h), which were higher than the 37% furfural yield in water.<sup>[45]</sup> In a similar study using a carbon-based catalyst synthesized from waste biomass, Antonyraj et al. optimized furfural and HMF production from xylose and fructose, respectively, in a MIBK/H<sub>2</sub>O (7:3 volume ratio) system. Sulfate-modified lignin derived catalysts had yields of up to 65% furfural (175 °C, 3 h) from xylose and 27% HMF (150 °C, 3 h) from fructose. With regeneration, the catalyst was recycled six times with minimal loss in activity.<sup>[46]</sup>

Mazzotta et al. showed the combined benefit of a carbon-based catalyst with both Brønsted and Lewis acidity by using a sulfonated carbonaceous TiO<sub>2</sub> catalyst (405 nm pore size) in a biphasic MTHF/H<sub>2</sub>O system. HMF yields of 59% were achieved from fructose (180 °C, 1 h) and 46% from glucose (180 °C, 2 h). The Lewis acidity of the TiO<sub>2</sub> isomerized glucose to fructose, allowing for increased activity, such as with cellobiose where 39% HMF yield was achieved (180 °C, 1 h). This sulfonated carbon-based catalyst also had 51% furfural from xylose (180 °C, 30 min).<sup>[47]</sup>

Increased partitioning of furfural to the organic phase with NaCl has been applied with carbon-based catalysts as well. Deng et al. demonstrated the use of a dichloromethane/H<sub>2</sub>O biphasic system to convert the xylose in concentrated pre-hydrolysis liquor (CPHL) of corncob to furfural. Using bio-char catalysts, CPHL containing 5 wt% xylose resulted in 81% furfural yield in the modified biphasic system compared to only 61% furfural without NaCl (170 °C; 1 h).<sup>[4]</sup> In another study with carbon-based catalysts, sulfonated nano-sized diamond powder was used by Delbecq et al. in a modified CPME/H<sub>2</sub>O biphasic system.<sup>[31]</sup> Similar to work done with polymer catalysts,<sup>[30]</sup> increasing the NaCl concentration increased the furfural yield, with a maximum furfural yields of 76% with 2 mM NaCl (200 °C, 50 min; Figure 2).<sup>[31]</sup>

Carbon-based catalysts resulted in high furfural yields likely due to the high surface area and acid functionality of the catalyst. The catalysts also have high thermal stability, are recyclable, and benefit from the addition of a modifier (NaCl). As with other catalysts discussed in this review, carbon-based catalysts also benefited from higher organic to aqueous ratios.

## 2.6. Other Catalysts

Although zeolites, polymer-based, niobium, and carbon catalysts are the most commonly reported heterogeneous catalysts used in biphasic systems in the past five years, researchers have

reported using other catalysts ranging from metal oxides to phosphate-based catalysts to produce furans.

Hydrothermally stable, supported metal oxide catalysts have been used for efficient one-pot furfural synthesis by Bhaumik and Dhepe in a toluene/H<sub>2</sub>O biphasic system,<sup>[48]</sup> similar to the one-pot method previously mentioned using H-USY zeolite.<sup>[19]</sup> Improving upon 54% furfural obtained with H-USY (170 °C; 6 h),<sup>[19]</sup> the reaction system with sol-gel-synthesized, silica-supported tungsten oxide catalysts yielded 71% furfural (170 °C; 10 h) from isolated xylan. Pentosane from various crop wastes yielded 72–87% furfural (170 °C; 8 h), which demonstrated the utility of the tungsten oxide catalysts.<sup>[48]</sup>

Metal oxide catalysts have also been used with phase modifiers to increase furfural yields in biphasic systems. Solid acid SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>-ZrO<sub>2</sub>/La<sup>3+</sup> was used as the catalyst by Li et al. in a modified biphasic system to convert xylose to furfural. Different aprotic organic solvents (DMSO, DMF, and 1,3-dimethyl-2-imidazolidinone) were added to the aqueous phase while the MIBK organic phase was modified with 2-butanol.<sup>[49]</sup> As was seen in work with Sn-MMT,<sup>[40]</sup> the addition of DMSO to the aqueous phase increased furfural yields. Adding 2-butanol to the 1,3-dimethyl-2-imidazolidinone organic layer resulted in approximately 12 times the yield of furfural compared to the system without modifiers; however, yields (34%) were still lower than compared to other catalyst systems. The polar aprotic solvents modifying the biphasic system did decrease side-reactions, improving furfural selectivity even though the reaction time was long.<sup>[49]</sup>

Aluminum oxides, in acidic, neutral, and basic forms, have been used with NaCl and CaCl<sub>2</sub> modifiers for the conversion of glucose to HMF in biphasic MIBK/H<sub>2</sub>O systems. As with the other heterogeneous catalysts reviewed, the NaCl modified system showed increased HMF yields, however, the highest yield, 52%, was observed with the acidic Al<sub>2</sub>O<sub>3</sub> in a CaCl<sub>2</sub> modified system (175 °C, 15 min). Garcia-Sanco et al. found that the addition of calcium cations favored  $\alpha$ -D-glucopyranose, confirmed by H-NMR, which potentially was more favorable for dehydration to HMF than  $\beta$ -D-glucopyranose.<sup>[50]</sup>

Another catalyst, inexpensive potassium aluminum sulfate (PA) with high porosity was used by Gupta et al. in biphasic systems for furan production. Increasing the reaction temperature from 140 °C to 190 °C (6 h) increased furfural yields from 5% to 55% from xylose, but further increasing the reaction time resulted in lower furfural yields due to furfural degradation. Using saturated NaCl as a modifier for HMF production increased HMF yields from 40% to 49% and 58% to 64% from glucose and fructose, respectively. As was seen with numerous other catalysts, the introduction of NaCl as a phase modifier increased HMF yields, which was attributed to the salting out effect.<sup>[51]</sup>

Another type of catalyst, chromium phosphate (CrPO<sub>4</sub>) has been used in biphasic THF/H<sub>2</sub>O systems modified with NaCl. The simultaneous optimization of both furfural and HMF (180 °C, 1.5 h) resulted in maximum yields of 67% and 32%, respectively. Although CrPO<sub>4</sub> is heterogeneous in nature, a filtered aqueous solution with solubilized CrPO<sub>4</sub> resulted in 57% furfural from xylose, suggesting a homogeneous reaction

may be the primary reaction mechanism.<sup>[52]</sup> In a similar study by Xia et al. to synthesize both furfural and HMF, biphasic THF/H<sub>2</sub>O systems modified with NaCl were used with FePO<sub>4</sub> and NaH<sub>2</sub>PO<sub>4</sub> as co-catalysts. For reactions at 150 °C and 1 h, furfural and HMF yields of 92% and 34%, respectively, were achieved; HMF yields increased to 44% at 160 °C and 1 h at the cost of decreasing furfural yields by 4%.<sup>[53]</sup> Despite this decrease in furfural yield, the NaCl modified THF/H<sub>2</sub>O biphasic system shows the potential for the simultaneous synthesis of furfural and HMF at reasonable yields. FePO<sub>4</sub> is soluble at the increased reaction temperatures and observed patterns of recrystallization suggested a possible contribution of a homogeneous reaction.<sup>[53]</sup>

In a true heterogeneous reaction, Alam et al. demonstrated titanium hydrogen phosphate with high acidity (1400  $\mu$ mol/g) for HMF production. In biphasic THF/H<sub>2</sub>O systems modified with NaCl, HMF yields of 55% from fructose and 35% from glucose were achieved. Reactions increasing the catalyst loading with fructose showed non-linear HMF trends, which indicates mass transport limitations associated with the heterogeneous catalyst.<sup>[54]</sup>

Unlike the previous phosphate-based catalysts, Dutta et al. used a mesoporous tin phosphate catalyst for HMF production in biphasic MIBK/H<sub>2</sub>O. This large pore (10.4 nm diameter) material achieved 50%, 39%, and 32% HMF from glucose, cellobiose, and cellulose, respectively (150 °C, 20 min). The addition of NaCl increased HMF partitioning into the organic phase via the salting-out effect, resulting in a 12% increase in HMF yield from glucose.<sup>[55]</sup>

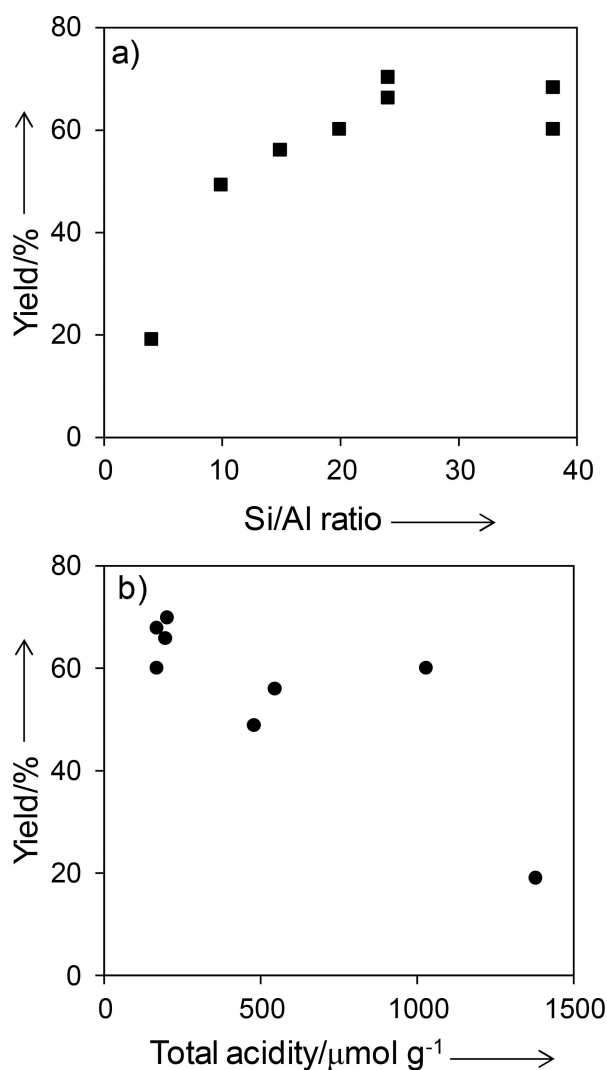
Metal-oxide, phosphate, and sulfate catalysts follow similar trends to the previously discussed catalysts. They benefited from the addition of a modifiers to the aqueous and organic phases as well as increased reaction temperatures, to a point.

## 2.7 Catalyst Summary

Numerous types of heterogeneous catalysts have been applied in biphasic systems producing high furan yields. When considering all of the data presented in this paper, several trends emerged based on catalyst type and across all catalysts.

For zeolites, correlations between the acidity and furfural yields were expected; however, the correlation did not trend as expected, which would have been that the yield increased with acidity. From the furfural yield data presented in Table 1 for zeolites, Figure 3a shows the positive correlation in furfural yield with increasing Si/Al ratio. (As previously mentioned, as the Si/Al ratio increases, the total acidity decreases.<sup>[16]</sup>) Below a Si/Al ratio of approximately 20, the furfural yield decreased with decreasing Si/Al ratio. Figure 3b shows that as the total acidity of the zeolite catalyst increased, the furfural yield decreased and that the highest yields were achieved at total acidities of less than 200  $\mu$ mol/g. Although Antunes et al. showed increasing acidity from 168  $\mu$ mol/g to 204  $\mu$ mol/g increased furfural yields by 10%,<sup>[20]</sup> considering all zeolites in Table 1, the high acidities may have resulted in furfural degradation reactions and unwanted by-products. This trend was also seen with clay





**Figure 3.** Correlations of furfural yields and a) Si/Al ratio and b) total acidity of the zeolites reported in Table 1.

and Nb-based catalysts. Li et al. reported that decreasing the acidity of MMT with the addition of tin (from 2050  $\mu\text{mol/g}$  to 1300  $\mu\text{mol/g}$ ) increased furfural yields by approximately 12%.<sup>[40]</sup> Additionally, Pholjaroen et al. saw 8% increase in furfural yields with lower acidity NbP (402  $\mu\text{mol/g}$ ) compared to ZrP (633  $\mu\text{mol/g}$ ).<sup>[17]</sup> No obvious trends in catalyst acidity arose with HMF production from zeolites investigated by Pande et al.<sup>[21]</sup> or supported niobium catalysts by Garcia-Sancho et al.<sup>[36]</sup>

Diffusion limitations with heterogeneous catalysts can also significantly affect their activity. Although inconsequential with macroporous ( $> 50$  nm) catalysts, such as ion exchange resins, the kinetic diameters of sugars, including xylose (0.68 nm<sup>[2]</sup>) and glucose (0.86 nm<sup>[2,56]</sup>), as well as furans (0.55–0.62 nm<sup>[56]</sup>) are of similar size to microporous ( $< 2$  nm) catalysts such as zeolites. Although some zeolite pore diameters are smaller than sugars, such as with H-MCM-22 (0.55 nm) which exhibited high activity,<sup>[20]</sup> molecules up to 0.2 nm<sup>[5]</sup> larger can diffuse into the crystalline structure.<sup>[25]</sup> Additionally, zeolites are flexible, especially at high temperatures, allowing the pores to flex and

molecules larger than the pore size to adsorb.<sup>[57]</sup> Even with high acidity, the limited diffusion of a reactant in a catalyst can decrease reactivity. For example, Pholjaroen et al. saw similar yields using high Lewis acid microporous zeolites, H-BEA (890  $\mu\text{mol/g}$ ; pore diameter: 0.74 nm) and H-Y (850  $\mu\text{mol/g}$ ; pore diameter: 0.61 nm), as they did with low Lewis acid site, phosphate-based mesoporous catalysts (220–300  $\mu\text{mol/g}$ ; pore diameter: 0.71–0.107 nm).<sup>[17]</sup> This could be due to the xylose being able to diffuse to the acid sites of the mesoporous catalyst more easily.

Improved mass transport in zeolites has been shown by introducing mesoporosity,<sup>[58]</sup> which was seen with mesoporous H-USY.<sup>[21]</sup> With larger pores, mesoporous materials have increased accessibility to acid sites resulting in increased activity.<sup>[16]</sup> For example, synthesized mesoporous Nb<sub>2</sub>O<sub>5</sub> showed approximately 20% increase in furfural yield from xylose (150 °C, 45 min) over commercial Nb<sub>2</sub>O<sub>5</sub>, attributed to the increased accessibility of xylose molecules to the acid sites in the pores.<sup>[35]</sup> This high activity is also seen with other mesoporous heterogeneous catalysts, such as Nb on silica support (SBA-15)<sup>[36]</sup> and tin phosphate.<sup>[55]</sup> In addition to mass transport benefits, mesoporous silicas, such as SBA-15, also have increased hydrothermal stability.<sup>[16,38]</sup> With higher furan yields resulting from mesoporous heterogeneous catalysts, biphasic systems have a unique potential to recover more product by preventing degradation and reducing the chance of pore blockage and product adsorption. The improved yields using mesoporous materials was shown using multiple catalyst types and multiple solvents, which is another important factor in biphasic reactions.

### 3. Solvent Selection

There are many properties to consider when choosing a solvent for biphasic systems. Toxicity, cost, viscosity, volatility, solubility of solute and carrier, the partition coefficient of the solute, and necessity of modifiers, amongst other properties, need to be balanced to find the most desirable solvent.<sup>[7]</sup> As seen in Table 5 (ordered by polarity), the solvents explored for synthesizing furans have a wide range of properties, but this table covers only a small fraction of considerations. More details and discussion about other properties have been discussed in other reviews and articles by Jessop et al.,<sup>[59]</sup> Sievers et al.,<sup>[58]</sup> and Knochel et al.<sup>[60]</sup> to name a few.

The most commonly used solvent for furfural extraction was toluene, which has low solubility in water and a low boiling point compared to both furfural (162 °C<sup>[61]</sup>) and HMF (291 °C<sup>[62]</sup>). The exceptionality of toluene as a solvent for furfural was demonstrated by Moreau et al.<sup>[63]</sup> and has further been supported by recent works, especially in the last five years. Due to their boiling points, toluene would be the top product in distillation, which leads to a lower purity furfural product. However, as the top product in distillation, high purity toluene would be preferred solvent reuse. For HMF, the most commonly researched solvent was MIBK, which gained popularity since Moreau et al. demonstrated its use as a solvent for HMF

**Table 5.** Properties of solvents used in this review.

Solvent	Boiling point [°C]	Melting point [°C]	Density [g/mL]	Water solubility [g/100 g]	Flash point [°C]	Polarity
p-Xylene	138.4	13.3	0.861	0.2	27	0.43 <sup>[59b]</sup>
1-Butanol	117.7	-88.6	0.8095	6.3	37	0.47 <sup>[59b]</sup>
o-Xylene	144	-25.2	0.897	0.17	32	0.48 <sup>[59b]</sup>
2-Propanol	82.4	-88.5	0.785	miscible	12	0.5 <sup>[59a]</sup>
Ethanol	78.5	-114.1	0.789	miscible	13	0.51 <sup>[59b]</sup>
2-Methyltetrahydrofuran (MTHF)	79	-20	0.86	14	-10	0.53 <sup>[59b]</sup>
Toluene	110.6	-93	0.867	0.05	4	0.55 <sup>[66]</sup>
Tetrahydrofuran (THF)	65	-108.4	0.8833	30	-14	0.6 <sup>[59a]</sup>
Methylisobutylketone (MIBK)	117	-80	0.8	2	14	0.63 <sup>[66]</sup>
gamma-Valerolactone (GVL)	207	-31	1.05	miscible	96	0.83 <sup>[67]</sup>
Dimethyl Sulfoxide (DMSO)	189	18.4	1.092	25.3	95	1 <sup>[68]</sup>
1,2-Dichloroethane	83.5	-35.7	1.245	0.861	13	n/a
2-Butanol	98	-115	0.808	miscible	27	n/a
Cyclopentyl methyl ether (CPME)	106	-140	n/a	0.3	-1	n/a
Cyclohexanol	161	21	0.948	3.6	68	n/a
1,3 Dimethyl-2-Imidazolidinone	225	7.5	1.056	miscible	95	n/a
2-sec-Butylphenol	227	12	0.982	0.15	112	n/a

production in 1994.<sup>[64]</sup> As with toluene and furfural, MIBK has a lower boiling point (117 °C<sup>[61]</sup>) than HMF, resulting in a lower purity HMF product. Additionally, MIBK has some solubility in water, which would need to be accounted for in the aqueous volume of the process. Another solvent used recently is SBP and even with low solubility in water, it is a less attractive solvent due to the difficulty of separating HMF and SBP as highlighted by Pagan-Torres et al.<sup>[65]</sup>

As an alternative processing method for when HMF and furfural are not the desired end products, the solvent can be selected to improve downstream processing. For example, Roman-Leshkov et al. used alcohols as the solvent and homogeneous catalysts to convert HMF to dimethylfuran over a CuRu based-catalyst. They found that toluene and MIBK were not inert in the hydrogenolysis reaction, but 1-butanol was. Additionally, 1-butanol can be produced from biomass.<sup>[69]</sup>

THF has been employed as an organic solvent in several biphasic systems<sup>[37–38,52–53]</sup> and in order to achieve sufficient phase separation, the use of NaCl (or other solvents or salts) as a modifier was necessary at the temperatures used. Modifiers added to monophasic systems can induce phase separation to biphasic systems and can be used to initiate the salting-out effect. NaCl is the most common modifier for heterogeneous catalytic systems and several papers demonstrated increased product yields with higher NaCl concentration.<sup>[29–31]</sup> For two different heterogeneous catalysts, one polymer-based the other carbon-based, an increase in furfural yield was observed when the concentration of NaCl was increased (Figure 2). This has also been observed with other polymer catalysts as well as clays.<sup>[30,40–41,44]</sup> Similar results have been observed for HMF with increasing NaCl concentration for modified biphasic systems.<sup>[26,50]</sup> The addition of modifiers increased partitioning of furans into the organic phase, and, in the case of a Nafion catalyst, created a synergetic catalytic effect that increased yields.<sup>[29]</sup> The addition of an aprotic organic solvent modifier to the organic phase has also shown the potential to increase furfural yields.<sup>[40,42]</sup> Researchers hypothesized that increasing solvent polarity with a modifier improved furfural yields,<sup>[70]</sup> but

when comparing the polarity values available in the literature (Table 5), there may be a lower limit versus “higher is better.”

Another consideration of solvent selection is the environmental friendliness of the solvent. For example, MTHF, a biorenewable solvent,<sup>[41]</sup> is a common choice for the organic solvent in biphasic systems. MTHF is an effective extractant, has good stability, and has a relatively low-cost.<sup>[47]</sup> Other solvents obtainable from biomass include GVL and 1-butanol.<sup>[69,71]</sup> The selection of an environmentally friendly solvent, and solvent in general, may be more attractive if the solvent is easy to recover and recycle or can be produced from the reaction products.

Unique to biphasic systems, increasing the organic to aqueous volume ratio increased furan yields.<sup>[17,28,32]</sup> This was likely due to the furans having a lower concentration in the aqueous phase, which reduces product degradation and decreased side reactions. Additionally, with heterogeneous catalysts, yields may be higher in biphasic systems since the extracting organic solvent may reduce pore-blockage on the catalyst surface from the products and humins.<sup>[32]</sup>

## 4. Conclusions and Outlook

There are many benefits to using biphasic systems for sugar and biomass reactions with the main benefit being increased furan yields. Biphasic media is favorable for the continuous extraction of furans during the reaction and using modifiers has been shown to improve yields in some cases.<sup>[11a]</sup> Additionally, biphasic systems could potentially reduce the energy demand associated with product recovery due to increased furan yields<sup>[5]</sup> and more concentrated products. Although aqueous systems are inexpensive and have historically shown moderate success for furan synthesis from lignocellulosic biomass, biphasic systems have shown significantly improved yields and selectivity towards furans using heterogeneous acid catalysts, including zeolites, oxides, and carbon-based catalysts among others. One setback of biphasic systems could arise in the

recovery of expensive extracting solvents, potentially reducing the economic advantages of the in situ extraction of furans.<sup>[5]</sup>

Producing furans in biphasic systems eliminates some of the issues seen in monophasic systems (e.g., furan degradation), but similar reaction trends still remain. Lower furan yields occurred at too high of acid concentrations, longer reaction times,<sup>[28]</sup> and high temperatures<sup>[44]</sup> due to side and degradation reactions. Too short of reaction time leads to incomplete xylose conversion<sup>[28]</sup> and too high of an initial xylose concentration also results in lower yields.<sup>[72]</sup>

The use of heterogeneous catalysts provides a unique opportunity to tailor the catalyst to the reaction. For example, glucose to HMF requires both Lewis and Brønsted acidity for the isomerization and dehydration reactions. Being able to tune the heterogeneous catalyst to have different acid sites and different ratios of acid sites opens the door to many different possibilities. However, chemical stability can be an issue and can lead to acid sites leaching and homogeneous reactions. Due to the benefits of biphasic systems and the ease of separating heterogeneous catalysts, these systems will likely play an important role in producing green chemicals from biomass in the future. However, further research is needed in order to understand the effect liquid systems have on heterogeneous catalysts and how solvent properties affect the reaction.

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## Conflict of Interest

The authors declare no conflict of interest.

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- [1] R. D. Perlack, L. L. Wright, A. F. Turhollow, R. L. Graham, B. J. Stokes, D. C. Erbach, Report No. DOE/GO-102005-2135, **2005**, Oak Ridge National Laboratory: Oak Ridge, TN.
- [2] S. M. Bruce, Z. Zong, A. Chatzidimitriou, L. E. Avci, J. Q. Bond, M. A. Carreon, S. G. Wettstein, *J. Mol. Catal. A* **2016**, *422*, 18–22.
- [3] a) N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapfle, M. Ladisch, *Bioresour. Technol.* **2005**, *96*, 673–686; b) C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapfle, M. R. Ladisch, Y. Y. Lee, *Bioresour. Technol.* **2005**, *96*, 1959–1966; c) R. Alamillo, M. Tucker, M. Chia, Y. Pagan-Torres, J. Dumesic, *Green Chem.* **2012**, *14*, 1413–1419; d) D. M. Alonso, J. Q. Bond, J. A. Dumesic, *Green Chem.* **2010**, *12*, 1493–1513; e) M. Balat, M. Balat, E. Kirtay, H. Balat, *Energy Convers. Manage.* **2009**, *50*, 3158–3168; f) J. Cheng *Biomass to renewable energy processes*, CRC Press, Boca Raton, **2010**; g) H. Li, J. F. Deng, *J. Chem. Technol. Biotechnol.* **2001**, *76*, 985–990; h) J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem. Int. Ed.* **2007**, *46*, 7164–7183; *Angew. Chem.* **2007**, *119*, 7298–7318; i) G. W. Huber, R. D. Cortright, J. A. Dumesic, *Angew. Chem. Int. Ed.* **2004**, *43*, 1549–1551; *Angew. Chem.* **2004**, *116*, 1575–1577; j) M. Cardenas-Fernandez, M. Bawn, C. Hamley-Bennett, P. K. V. Bharat, F. Subrizi, N. Suhaili, D. P. Ward, S. Bourdin, P. A. Dalby, H. C. Hailes, P. Hewitson, S. Ignatova, C. Kontoravdi, D. J. Leak, N. Shah, T. D. Sheppard, J. M. Ward, G. J. Lye, *Faraday Discuss.* **2017**, *202*, 415–431; k) I. Wheelodon, P. Christopher, H. Blanch, *Curr. Opin. Biotechnol.* **2017**, *45*, 127–135.
- [4] A. Deng, Q. Lin, Y. Yan, H. Li, J. Ren, C. Liu, R. Sun, *Bioresour. Technol.* **2016**, *216*, 754–760.
- [5] J.-P. Lange, E. van der Heide, J. van Buijtenen, R. Price, *ChemSusChem* **2012**, *5*, 150–166.
- [6] a) M. A. Mellmer, C. Sener, J. M. R. Gallo, J. S. Luterbacher, D. M. Alonso, J. A. Dumesic, *Angew. Chem. Int. Ed.* **2014**, *126*, 12066–12069; b) M. A. Mellmer, C. Sanpitakseree, B. Demir, P. Bai, K. Ma, M. Neurock, J. A. Dumesic, *Nat. Catal.* **2018**, *1*, 199–207.
- [7] J. D. Seader, E. J. Henley, D. K. Roper *Separation Process Principles with Applications Using Process Simulators*, 4th ed., Wiley, **2016**.
- [8] a) R. A. Sheldon, *Green Chem.* **2005**, *7*, 267–278; b) J. Viell, A. Harwardt, J. Seiler, W. Marquardt, *Bioresour. Technol.* **2013**, *150*, 89–97.
- [9] a) G. Dinesh, S. Basudeb, B. Asim, *ChemSusChem* **2014**, *7*, 2342–2350; b) B. Agarwal, K. Kailasam, R. S. Sangwan, S. Elumalai, *Renewable Sustainable Energy Rev.* **2018**, *82*, 2408–2425.
- [10] H. Hoydonckx, W. Van Rhijn, W. Van Rhijn, D. De Vos, P. Jacobs *Ullmann's encyclopedia of industrial chemistry* **2000**.
- [11] a) S. Dutta, S. De, B. Saha, M. I. Alam, *Catal. Sci. Technol.* **2012**, *2*, 2025–2036; b) R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev.* **2013**, *113*, 1499–1597; c) D. W. Rackemann, W. O. S. Doherty, *Biofuels Bioprod. Biorefin.* **2011**, *5*, 198–214.
- [12] F. Delbecq, Y. Wang, A. Muralidhara, K. E. Ouardi, G. Marlair, C. Len, *Front. Chem.* **2018**, *6*.
- [13] B. Trewyn *Heterogeneous Catalysis for Today's Challenges: Synthesis, Characterization and Applications*, Royal Society of Chemistry, **2015**.
- [14] F. Liu, K. Huang, A. Zheng, F.-S. Xiao, S. Dai, *ACS Catal.* **2018**, *8*, 372–391.
- [15] T. Ennaert, J. Van Aelst, J. Dijkmans, R. De Clercq, W. Schutyser, M. Dusselier, D. Verboekend, B. F. Sels, *Chem. Soc. Rev.* **2016**, *45*, 584–611.
- [16] S. De, S. Dutta, B. Saha, *Catal. Sci. Technol.* **2016**, *6*, 7364–7385.
- [17] B. Pholjaroen, N. Li, Z. Wang, A. Wang, T. Zhang, *J. Energy Chem.* **2013**, *22*, 826–832.
- [18] K. Yoshida, H. Nanao, Y. Kiyozumi, K. Sato, O. Sato, A. Yamaguchi, M. Shirai, *J. Taiwan Inst. Chem. Eng.* **2017**, *79*, 55–59.
- [19] R. Sahu, P. L. Dhepe, *ChemSusChem* **2012**, *5*, 751–761.
- [20] M. M. Antunes, S. Lima, A. Fernandes, M. Pillinger, M. F. Ribeiro, A. A. Valente, *Appl. Catal. A* **2012**, *417*, 243–252.
- [21] A. Pande, P. Niphadkar, K. Pandare, V. Bokade, *Energy Fuels* **2018**, *32*, 3783–3791.
- [22] C. Baerlocher and L. B. McCusker, Database of Zeolite Structures, <http://www.iza-structure.org/databases/>.
- [23] J. Jow, G. L. Rorrer, M. C. Hawley, D. T. A. Lampert, *Biomass* **1987**, *14*, 185–194.
- [24] V. V. Ordomsky, J. van der Schaaf, J. C. Schouten, T. A. Nijhuis, *J. Catal.* **2012**, *287*, 68–75.
- [25] L. L. Hegedus, A. T. Bell, N. Y. Chen, W. O. Haag, J. Wei, R. Aris, M. Boudart, B. C. Gates, G. A. Somorjai, *Catalyst Design-Progress and Perspectives*, Wiley-Interscience, New York, **1988**.
- [26] D. W. Gardner, J. Huo, T. C. Hoff, R. L. Johnson, B. H. Shanks, J.-P. Tessonnier, *ACS Catal.* **2015**, *5*, 4418–4422.
- [27] a) B. M. Antunes, A. E. Rodrigues, Z. Lin, I. Portugal, C. M. Silva, *Fuel Process. Technol.* **2015**, *138*, 86–99; b) B. Das, P. Thirupathi, I. Mahender, V. S. Reddy, Y. K. Rao, *J. Mol. Catal. A* **2006**, *247*, 233–239.
- [28] A. Mittal, S. K. Black, T. B. Vinzant, M. O'Brien, M. P. Tucker, D. K. Johnson, *ACS Sustainable Chem. Eng.* **2017**, *5*.
- [29] S. Le Guenic, D. Gergela, C. Ceballos, F. Delbecq, C. Len, *Molecules* **2016**, *21*, 1102.
- [30] Y. Wang, T. Len, Y. Huang, A. Diego Taboada, A. N. Boa, C. Ceballos, F. Delbecq, G. Mackenzie, C. Len, *ACS Sustainable Chem. Eng.* **2017**, *5*, 392–398.
- [31] F. Delbecq, Y. Takahashi, T. Kondo, C. C. Corbas, E. R. Ramos, C. Len, *Catal. Commun.* **2018**, *110*, 74–78.
- [32] V. V. Ordomsky, J. van der Schaaf, J. C. Schouten, T. A. Nijhuis, *ChemSusChem* **2012**, *5*, 1812–1819.
- [33] F. Yang, Q. Liu, X. Bai, Y. Du, *Bioresour. Technol.* **2011**, *102*, 3424–3429.
- [34] M. J. C. Molina, M. L. Granados, A. Gervasini, P. Carniti, *Catal. Today* **2015**, *254*, 90–98.
- [35] C. García-Sancho, J. M. Rubio-Caballero, J. M. Mérida-Robles, R. Moreno-Tost, J. Santamaría-González, P. Maireles-Torres, *Catal. Today* **2014**, *234*, 119–124.

- [36] C. García-Sancho, I. Agirrezabal-Telleria, M. B. Güemez, P. Maireles-Torres, *Appl. Catal. B* **2014**, 152–153, 1–10.
- [37] N. K. Gupta, A. Fukuoka, K. Nakajima, *ACS Catal.* **2017**, 7, 2430–2436.
- [38] K. Peng, X. Li, X. Liu, Y. Wang, *Mol. Catal.* **2017**, 441, 72–80.
- [39] H. Nanao, H. Amanuma, K. Yoshida, O. Sato, A. Yamaguchi, M. Shirai, *Clay Sci.* **2017**, 21, 35–39.
- [40] H. Li, J. Ren, L. Zhong, R. Sun, L. Liang, *Bioresour. Technol.* **2015**, 176, 242–248.
- [41] Q. Lin, H. Li, X. Wang, L. Jian, J. Ren, C. Liu, R. Sun, *Catalysts* **2017**, 7, 118.
- [42] H. Li, X. Chen, J. Ren, H. Deng, F. Peng, R. Sun, *Biotechnol. Biofuels* **2015**, 8.
- [43] H. Li, Q. Dai, J. Ren, L. Jian, F. Peng, R. Sun, G. Liu, *Carbohydr. Polym.* **2016**, 136, 203–209.
- [44] Q. Qing, Q. Guo, L. Zhou, Y. Wan, Y. Xu, H. Ji, X. Gao, Y. Zhang, *Bioresour. Technol.* **2017**, 226, 247–254.
- [45] Y. Wang, F. Delbecq, W. Kwapinski, C. Len, *Mol. Catal.* **2017**, 438, 167–172.
- [46] C. A. Antonyraj, A. Haridas, *Catal. Commun.* **2018**, 104, 101–105.
- [47] M. G. Mazzotta, D. Gupta, B. Saha, A. K. Patra, A. Bhaumik, M. M. Abu-Omar, *ChemSusChem* **2014**, 7, 2342–2350.
- [48] P. Bhaumik, P. L. Dhepe, *ChemCatChem* **2017**, 9, 2709–2716.
- [49] H. Li, A. Deng, J. Ren, C. Liu, W. Wang, F. Peng, R. Sun, *Catal. Today* **2014**, 234, 251–256.
- [50] C. García-Sancho, I. Fúnez-Núñez, R. Moreno-Tost, J. Santamaría-González, E. Pérez-Inestrosa, J. Fierro, P. Maireles-Torres, *Appl. Catal. B* **2017**, 206, 617–625.
- [51] D. Gupta, E. Ahmad, K. K. Pant, B. Saha, *RSC Adv.* **2017**, 7, 41973–41979.
- [52] S. Xu, D. Pan, Y. Wu, X. Song, L. Gao, W. Li, L. Das, G. Xiao, *Fuel Process. Technol.* **2018**, 175, 90–96.
- [53] H. Xia, S. Xu, L. Yang, *RSC Adv.* **2017**, 7, 1200–1205.
- [54] M. I. Alam, S. De, B. Singh, B. Saha, M. M. Abu-Omar, *Appl. Catal. A* **2014**, 486, 42–48.
- [55] D. Arghya, G. Dinesh, P. A. K. S. Basudeb, B. Asim, *ChemSusChem* **2014**, 7, 925–933.
- [56] J. Jae, G. A. Tompsett, A. J. Foster, K. D. Hammond, S. M. Auerbach, R. F. Lobo, G. W. Huber, *J. Catal.* **2011**, 279, 257–268.
- [57] B. Ilić, S. G. Wettstein, *Microporous Mesoporous Mater.* **2017**, 239, 221–234.
- [58] C. Sievers, Y. Noda, L. Qi, E. M. Albuquerque, R. M. Rioux, S. L. Scott, *ACS Catal.* **2016**, 6, 8286–8307.
- [59] a) W. J. Cheong, P. W. Carr, *Anal. Chem.* **1988**, 60, 820–826; b) P. G. Jessop, D. A. Jessop, D. Fu, L. Phan, *Green Chem.* **2012**, 14, 1245–1259.
- [60] P. Knochel, (Ed.: P. Knochel), Berlin, Heidelberg : Springer Berlin Heidelberg, **1999**.
- [61] Material Safety Data Sheets, accessed 5/2018, Available electronically at <http://www.sigmaaldrich.com>.
- [62] X. Kong, R. Zheng, Y. Zhu, G. Ding, Y. Zhu, Y.-W. Li, *Green Chem.* **2015**, 17, 2504–2514.
- [63] C. Moreau, R. Durand, D. Peyron, J. Duhamet, P. Rivalier, *Ind. Crops Prod.* **1998**, 7, 95–99.
- [64] C. Moreau, R. Durand, C. Pourcheron, S. Razigade, *Ind. Crops Prod.* **1994**, 3, 85–90.
- [65] Y. J. Pagan-Torres, T. F. Wang, J. M. R. Gallo, B. H. Shanks, J. A. Dumesic, *ACS Catal.* **2012**, 2, 930–934.
- [66] D. C. Leggett, *Anal. Chem.* **1993**, 65, 2907–2909.
- [67] A. Duereh, Y. Sato, R. L. Smith, H. Inomata, *J. Phys. Chem. B* **2016**, 120, 4467–4481.
- [68] L. Crowhurst, R. Falcone, N. L. Lancaster, V. Llopis-Mestre, T. Welton, *J. Org. Chem.* **2006**, 71, 8847–8853.
- [69] Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* **2007**, 447, 982–U985.
- [70] T. Yang, Y. H. Zhou, S. Z. Zhu, H. Pan, Y. B. Huang, *ChemSusChem* **2017**, 10, 4066–4079.
- [71] D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Green Chem.* **2013**, 15, 584–595.
- [72] E. I. Gürbüz, S. G. Wettstein, J. A. Dumesic, *ChemSusChem* **2012**, 5, 383–387.

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