

Review

The Role of Ionic Liquids on Biomass Liquefaction—A Short Review of the Recent Advances

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Abstract: Biomass is recognised as one of the most attractive feedstocks among the alternative resources, having a high potential for the sustainable production of valuable chemicals and biofuels. Due to its abundance, convenience, carbon neutrality and eco-friendliness, biomass is believed to positively impact the current environmental crisis caused by the extensive use of petroleum resources. For this reason, the search for processes that can convert this feedstock, resolving some inherent drawbacks, is needed. Biomass liquefaction using ionic liquids (ILs) as catalysts has received appreciable attention in renewable fuels and chemicals production. With the potential for a substantial number of anion and cation pairings, ILs can be an attractive medium towards reusability and sustainability for these processes due to the unique and tunable combinations of their functional groups and, therefore, their properties. In this review, several studies using ILs in biomass liquefaction are compared and discussed. With a particular emphasis on the last five years, advantages and disadvantages will be discussed using this class of liquids addressing essential issues such as yields, reusability and conversion, among others.

Keywords: biomass; liquefaction; ionic liquids; solvent; catalyst



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1. Introduction

Our modern lifestyle, as we know it, is about to change. Oil depletion is becoming a reality. A change in the present economic and industrial paradigm, based on petroleum feedstock, is vital.

Biomass is recognised as one of the most attractive feedstocks among the alternative resources, having a high potential for the sustainable production of valuable chemicals and biofuels. Due to its abundance, convenience, carbon neutrality and eco-friendliness, biomass is believed to positively impact the current environmental crisis caused by the extensive use of petroleum resources.

According to the directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, 'biomass' means the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste. This definition emphasises the several biomass resources available that can be converted to added-value products or fuels. Vassilev and co-workers [1] have established a general classification of biomass, establishing several groups and subgroups according to source and origin (Figure 1).

Biomass conversion methods can be divided into thermochemical and biochemical methods. In thermochemical methods, the thermal depolymerisation of biomass can be

conducted using various technologies. Pyrolysis, gasification and hydrothermal processing are widely used to produce fuels and valuable chemicals [2].



Figure 1. General classification of biomass according to Vassilev and co-workers [1].

There are several drawbacks related to the use of biomass feedstocks in some of these processes. Such drawbacks include the high moisture content, which requires energy-intensive pretreatment before it can be used. The failure to identify some of the compounds formed during these processes is also an issue, mainly because of the lack of gas chromatography-mass spectrometry (GC-MS) library matching identifications, often linked to produced complex mixtures with unstable compounds [3]. For these reasons, biomass liquefaction using ionic liquids (ILs) as catalysts has received appreciable attention in renewable fuels and chemicals production.

With the potential for a substantial number of anion and cation pairings, ILs can be an attractive medium towards reusability and sustainability for these processes due to the unique and tunable combinations of their functional groups-and, therefore, their properties. There are several classes of homogeneous and heterogeneous ILs (Figure 2). However, issues such as production costs, long synthetic routes, disputed biodegradability and the use of volatile solvents are undeniably barriers hindering them from being considered as emerging solvents for several applications.

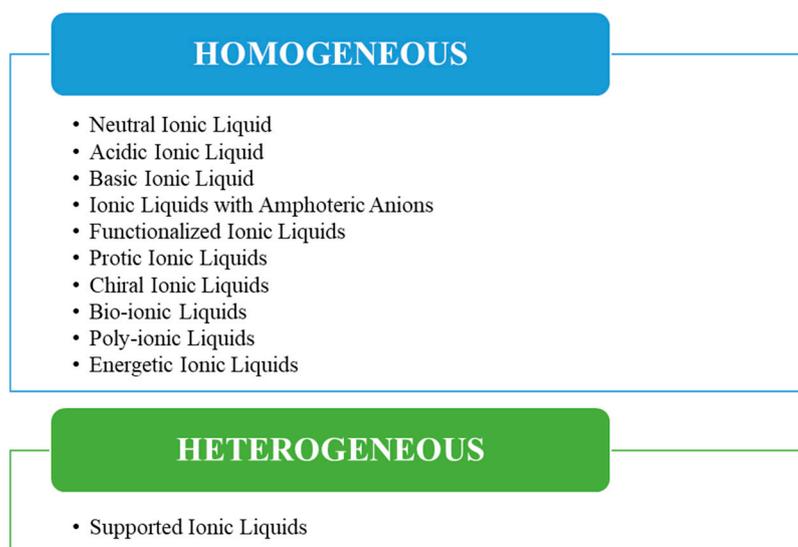


Figure 2. Classes of homogeneous and heterogeneous ILs.

However, as addressed by Tom Weldon [4] in his brief history, the research with ionic liquids conducted by many thousands of people is compared to a great river, where there is still much research to be developed. Since ionic liquids are a field of study continuously growing in size in their variety and applications, Weldon states that it is challenging to find an expert mastering the whole subject once most researchers focus only on few IL applications or a subset of their physical properties.

Over the years, the number of publications concerning this class of catalysts has grown exponentially. In the past five years, almost 55,000 publications refer to ILs. Different areas use this subject (Table 1), the physical-chemistry area being the most representative.

Table 1. Top 10 most representative areas concerning the Ionic Liquids subject for the last five years.

Position	Field: Web of Science Categories	% of 54,981
1	Chemistry physical	26.7%
2	Chemistry multidisciplinary	24.6%
3	Materials science multidisciplinary	15.0%
4	Engineering chemical	14.6%
5	Physics atomic molecular chemical	8.2%
6	Chemistry analytical	7.4%
7	Electrochemistry	6.9%
8	Energy fuels	6.8%
9	Polymer science	6.6%
10	Nanoscience nanotechnology	6.4%

When we refine the results for the liquefaction subject, the number diminishes drastically, being Engineering Chemistry and Energy Fuels the main areas. Despite the increasing behaviour of the Energy Fuels area in the last years, it is still reduced proportion justifying the need for more studies.

In this review, several studies using ILs as catalysts in biomass liquefaction are compared and discussed. With special emphasis on research conducted in the last five years, biomass conversion liquefaction will be addressed per type of biomass, where comparisons will be made through yields and conversion rates for each IL.

2. Biomass Liquefaction with Ionic Liquids

2.1. Wood and Woody Biomass

The supply of wood and woody biomass for energy is intrinsically connected to several industries. However, this type of biomass is not restricted to industrial sources.

Annually, forests represent an important source, with all the removals that consider the volume of all trees (living or dead) and natural losses such as branches that can be retrieved. Despite this, many wood-based products can also be recycled, becoming another important source. Several liquefaction studies use this resource, with extensive data to be found in the archives.

Lu et al. [5] explored green and efficient ways to convert fir sawdust (41.01% cellulose, 27.09% hemicellulose, 30.24% acid-insoluble lignin and 1.66% ash) taken from a wood processing factory into sustainable energy and chemicals. Lu and his team first investigated biomass liquefaction using a polyethylene glycol 400 (PEG400)-glycerol mixture at atmospheric pressure with an Acidic Ionic Liquid (AIL) catalyst. Using 10 g of sawdust, 60 g of solvent, for 60 min at 150 °C with different catalysts concentrations (0.1–0.9 mol·L⁻¹), the authors investigated the effect of four kinds of Brønsted acidic ionic liquids (BAILs) with different cations, 1-methylimidazolium hydrogensulfate ([mim][HSO₄]), 1-butyl-3-methylimidazolium hydrogensulfate ([bmim][HSO₄]), 1-(3-sulfopropyl)-3-methylimidazolium hydrogensulfate ([SO₃Hpmim][HSO₄]) and 1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate ([SO₃Hbmim][HSO₄]) in the liquefaction of this type of biomass, taking sulphuric acid (H₂SO₄) as a comparison. By introducing the sulfoalkyl substituent into the imidazolium cation of AIL, the authors significantly improved its catalytic activity with concentrations between 0.3 and 0.9 mol·L⁻¹, obtaining a liquefaction yield (99%) similar to the one obtained with H₂SO₄. This was attributed to the presence of double acid sites in [SO₃Hbmim][HSO₄] and [SO₃Hpmim][HSO₄], more similar to H₂SO₄ when compared with the single ones present in [bmim][HSO₄] and [mim][HSO₄], giving the following order according to its catalytic performance: [SO₃Hbmim][HSO₄] ≈ [SO₃Hpmim][HSO₄] > [bmim][HSO₄] > [mim][HSO₄].

By the Fourier-transform infrared spectroscopy (FTIR) spectra comparison, the authors identified aromatic moieties from lignin degradation on the heavy oil, contrary to those present in the light oil derived from cellulose. In terms of composition, 90 wt.% of the bio-oil was found to be heavy oil.

Grilc and co-workers [6], for the same purpose, conducted experiments with a different feedstock, sawdust from debarked European beech (*Fagus sylvatica*) composed of cellulose, hemicellulose and lignin with the weight contents of 39.4, 33.3 and 24.8%, respectively. The research group evaluated the solvolysis of wood and its main components (cellulose, hemicellulose and lignin) in glycerol, with five homogeneous imidazolium-based IL catalysts aiding the process. [bmim][HSO₄], 1-butyl-3-methylimidazoliumacetate ([bmim][CH₃COO]), 1-butyl-3-methylimidazolium chloride-aluminum chloride ([bmim][Cl/AlCl₃]), 1-ethyl-3-methylimidazolium chloride-aluminum chloride ([emim][Cl/AlCl₃]) and 1-allyl-3-methylimidazolium chloride-aluminum chloride ([amim][Cl/AlCl₃]) were selected in order to compare both cation chain length and anion substitution influence. The authors found that the length and type of side chain on the imidazolium cation was less important than the anion selection. However, the acidity of the anions acetate and sulphate was clearly insufficient to catalyse the solvolysis since the authors retrieve almost the same mass of insoluble residue. The best conversion rates were obtained for [bmim][Cl/AlCl₃] within a 60 min reaction time, reaching 64.4 and 91.5 wt.% for 150 and 200 °C, respectively, supporting the premises that the anion plays the vital role. When compared with the results of Lu et al. [5], identical conversion yields were obtained, however, occurring at higher temperatures.

With smaller liquefaction yields 43–75%, Wu and co-workers [7] studied a similar type of biomass, *Eucalyptus grandis* sawdust obtained from a wood processing factory, with higher cellulose percentage (47.9% cellulose, 71.2% holocellulose, 27.1% Klason lignin and 0.29% ash) to obtain microcrystalline cellulose (MCC). The authors used 10 g of sawdust and 80 g of ethylene glycol with different catalyst amounts, [SO₃Hbmim][HSO₄] (0.1–0.3 mmol·g⁻¹), temperatures ranging between 140 and 180 °C and reaction times between 15 and 90 min. The research team concluded that raising the temperature, prolonging the time or increasing the catalyst often facilitates the breakage of the glycosidic bonds

of cellulose chains, impacting the cellulose yield and reducing the degree of polymerization (DP). However, with a $0.2 \text{ mmol}\cdot\text{g}^{-1}$ of catalyst at $180 \text{ }^\circ\text{C}$, the cellulose DP did not change significantly over time. 79% MCC was obtained through incomplete liquefaction at atmospheric pressure.

Liu and co-workers [8] evaluated the catalytic hydro-liquefaction of sawdust and its three components (cellulose, hemicellulose and lignin) under reductive pressure (H_2). The authors studied several reactional systems containing sawdust, ethanol, 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and nickel chloride (NiCl_2). Five different reactional systems were considered (Sawdust; Sawdust/ethanol; Sawdust/ethanol/[bmim][Cl]; Sawdust/ethanol/ NiCl_2 and Sawdust/ethanol/ NiCl_2 /[bmim][Cl]), under different temperatures (295 to $400 \text{ }^\circ\text{C}$) and hydrogen pressures (2 to 10 MPa). The authors found that the maximum sawdust conversion of 69.8% and liquid yield of 49.5% of bio-oil was obtained using [bmim][Cl]/ NiCl_2 as a catalyst with supercritical ethanol. These findings suggested that using an ionic liquid nickel catalyst with supercritical ethanol had a synergistic effect on the sawdust conversion. Two studies were conducted regarding the effect of temperature, ranging from 295 to $360 \text{ }^\circ\text{C}$ for hydro-liquefaction of sawdust, cellulose and hemicellulose and temperatures from 300 to $400 \text{ }^\circ\text{C}$ for lignin conversion. A rapid decrease in the bio-oil yield was observed for temperatures above $320 \text{ }^\circ\text{C}$, with this being set as the optimal temperature. Lastly, the authors observed a positive effect of initial hydrogen pressure on sawdust conversion. The higher value tested (10 MPa) led to higher conversion, positively affecting the bio-oil yield.

To better describe the relationship between ionic liquid composition and catalytic performance, Li and co-workers [9] continued to study the NiCl_2 as a catalyst combined with different ionic liquids such as 1-butyl-3-methylimidazolium bromide ([bmim][Br]), [bmim][Cl], 1-ethyl-3-methylimidazolium chloride ([emim][Cl]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) in ethanol. A significant increase both in sawdust conversion (83.11%) and liquid yield (52.38%) was obtained with NiCl_2 and [bmim][Br] as a catalytic system. In contrast, the catalytic activity of NiCl_2 in [bmim][BF₄] was the lowest, suggesting what previous authors had already concluded, that the anion played a vital role in the sawdust hydro-liquefaction. The impact index defined by the authors to evaluate the performance of the catalytic system showed that the most significant impact index was obtained for 1-butyl-3-methylimidazolium bromide-nickel chloride ([bmim][Br]/ NiCl_2), being in good agreement with its excellent catalytic liquefaction performance. The authors believe that the type of ionic liquid in the catalytic system had no significant influence on the chemical compositions of oil.

Having that in mind and despite the identical FTIR spectra obtained, the authors found that by using the [bmim][Br]/ NiCl_2 catalytic system, there was enhanced dehydration and decarboxylation reactions due to its lowest O/C ratio. The highest H/C ratio was also achieved for this catalytic system, indicating that an improvement was also obtained in the hydrogenation reaction, proving its highest performance in the thermal degradation of sawdust. Finally, the quality of these bio-oils was justified by their higher heating values.

To study the efficiency of different pyridinium and imidazolium-based IL-water mixtures in the liquefaction of biomass, Yoshioka et al. [10] studied 12 IL/water combinations. These studies included: pyridinium chloride ([py][Cl]), pyridinium p-toluenesulfonate, 1-ethylpyridinium chloride, imidazolium chloride, 1-methylimidazolium chloride ([mim][Cl]), 1-methylimidazolium hydrogen sulfate, hydrazinium chloride, guanidinium chloride, pyridinium bromide and piperidinium chloride ionic liquids. Japanese cedar (*Cryptomeria japonica*) was treated with these IL-water mixtures at $120 \text{ }^\circ\text{C}$ for one hour to produce 5-hydroxymethylfurfural, furfural and 2-hydroxyacetylfuran (2-HAF). According to the authors, this work was the first to report 2-HAF in liquefied lignocellulosic biomass in the presence of ILs. All three compounds were identified in IL-water mixture containing pyridinium or imidazolium salts. The optimal IL-water mixture was a 10% water *w/w* solution and 90% [py][Cl].

Further studies were carried out in the work of Yoshioka et al. [11] with 1-ethyl-3-methylimidazolium acetate ([emim][CH₃COO]); [emim][Cl]; 1-ethyl-3-methylimidazolium hydrogensulfate ([emim][HSO₄]); 1-ethyl-3-methylimidazolium methanesulfonate; 1-ethyl-3-methylimidazolium p-toluenesulfonate; 1-ethylpyridinium bromide; 1-ethylpyridinium chloride; 1-ethylpyridinium iodide; [mim][Cl]; [mim][HSO₄]; [py][Cl]; pyridinium p-toluenesulfonate; tetrabutylammonium salicylate ionic liquids. Once again, the authors found that the 90% [py][Cl] and 10% water *w/w* solution was the most effective for the treatment of lignocellulosics to produce useful low molecular weight compounds, according to the different yields obtained. Hemicellulose was firstly liquefied, followed by lignin in the treatments of *C. japonica* with 90% [py][Cl] in water at 80 and 120 °C. In such conditions, most of the cellulose was still insoluble.

In Table 2 the ideal conditions for all the studies mentioned above are presented. Some factors can be used to compare such studies, such as the type of IL; IL dosage; the solvent(s) used, conditions (temperature and reaction time) to discuss the obtained yields further. However, these studies often lack information, such as how the IL dosage was considered or even about the purity of the IL used and how this affects its performance. In addition, different values of concentrations can be seen in such studies, some impossible to convert to more applied units, limiting progress in obtaining real conclusions about the efficiency of such IL catalyst on liquefaction. The amount from which an IL is considered a solvent and not a catalyst is not addressed in any of these studies, being also an important issue. Despite this, there is a tendency on the usage of two types of anions, the [HSO₄] and [Cl], due to its acidic nature, being [HSO₄] far more promising when in conjunction with [SO₃Hpmim] or [SO₃Hbmim] cations.

Table 2. Ideal conditions {Type of IL; ILs dosage; solvent(s); temperature (T); reaction time (Rt)} presented by different studies on the usage of ILs as catalysts or solvents on sawdust biomass liquefaction.

IL	IL Dosage	Solvent(s)	Conditions		Yield wt. %	Ref.
			T/°C	Rt/Min		
[SO ₃ Hpmim][HSO ₄] [SO ₃ Hbmim][HSO ₄]	0.3–0.9 mol·L ⁻¹	PEG 400 + glycerol (4:1 <i>w/w</i>)	150	60	<99	[5]
[bmim][Cl]/AlCl ₃	10 wt. %	Glycerol	150 200	60	66.4 91.5	[6]
[SO ₃ Hbmim][HSO ₄]	0.2 mmol·g ⁻¹	ethylene glycol	180	30 60 90	69.9 73.8 74.9	[7]
[bmim][Cl]/NiCl ₂	1.2 wt. % IL + 300 µg/g NiCl ₂	Supercritical ethanol	320	30	69.8	[8]
[bmim][Br]/NiCl ₂	1 wt. % IL + 300 µg/g NiCl ₂	Ethanol	320	30	83.1	[9]
[py][Cl]	90 wt. % IL/10 wt. % water	water	120	60	n.d.	[10,11]

n.d.—not defined by the author.

2.2. Herbaceous and Agricultural Biomass

Herbaceous and agriculture biomass is probably in the top 3 regarding the importance of biomass supply in the world. Generally, it comprises all non-woody plants and residues coming from agricultural lands, regardless of the chemical composition (i.e., lignocellulosic, starch, oil crops, etc.) and whether or not it is edible (i.e., food and energy crops) [12].

An excellent example of this type of biomass is the wheat straw due to its attractive application as feedstock for second-generation ethanol production, complementing wheat production rather than competing with its production. Despite this, the difficulty associated with its complex structure limits its conversion to added-value products, being a good candidate for liquefaction using ILs [13].

In the work of Baofeng and co-workers [14], hydrothermal liquefaction of wheat straw was performed with water/ethanol mixtures (at a ratio of 1:1, *v/v*) or sub-critical water

and others with the addition of [bmim][Cl] for comparison on the effect of such type of IL as a catalyst. The authors found that during hydrothermal liquefaction of wheat straw in the presence of sub-critical water at a temperature of 320 °C and a residence time of 30 min, without the addition of the ionic liquid [bmim][Cl], the maximum yield of oil was 22.7%, reached at 1 MPa. The maximum yield of gas was 41.3% and was reached at 2 MPa, while the maximum total conversion reached was 80.4% at 4 MPa. With the addition of the ionic liquid, the maximum yield of oil reached was 18.1% at 3 MPa; the maximum yield of gas and total conversion reached was 51% and 86.6%, respectively, at 2 MPa. The authors concluded that the addition of this ionic liquid would decrease the liquefaction residue, increasing gas yield. Concerning the oil yield, despite the authors correlating its increase with the presence of the [bmim][Cl], this is not clear in the results. There is not a typical behavior between the oil yield with or without [bmim][Cl] at the same pressure. The authors state that the ionic liquid [bmim][Cl] had a pronounced effect on product distribution during the liquefaction process. Its addition would contribute to the formation of new and longer polymers for longer reaction times, more than 30 min, decreasing the total conversion yield.

It was also found that the addition of [bmim][Cl] would increase not only the total conversion and gas yield but also the contents of the aliphatic hydrogen and phenols in liquid oil, improving its quality, reducing residue yield.

In the work of Guan et al. [13], apart from [bmim][Cl], two other ILs were used in the liquefaction of wheat straw to produce ethyl levulinate (EL), [bmim][HSO₄] and [SO₃Hbmim][HSO₄]. Using a one-pot reaction under mild conditions in ethanol, which served as both solvent and reactant, the authors concluded that [SO₃Hbmim][HSO₄] was the most effective catalyst, with a conversion rate of wheat straw of 85.8% when compared to the 22.0% and 36.7% values obtained for [bmim][Cl] and [bmim][HSO₄], respectively. This would indicate that the [Cl] anion was less effective than the [HSO₄] anion at dissolving and converting wheat straw. Correspondingly, the [bmim] cation had a lower effect than the one functionalized with a sulfonic acid moiety.

Assuming [SO₃Hbmim][HSO₄] as the best catalyst, the effects of amount of IL (0–54%) and reaction temperature (180–220 °C) and time (30–120 min) on conversion rates and yields of ethyl levulinate were studied. Concerning IL amount, an optimal amount of 26% IL increased the conversion of wheat straw and yield of EL from 22.33% and 6.23% (without IL) to 75.33% and 14.59%, respectively. The temperature increase favored the EL conversion and yield, up to 200 °C, reaching a maximum of 85.50% and 16.23%, respectively. Higher temperatures were found to produce further transformations of EL, increasing the amount of residues. Similar behavior was observed for the increase of reaction time. An increase in EL conversion and yield was observed until a reaction time of 60 min, decreasing after that. The authors justify this behavior with the possibility that below 60 min, the cellulose, hemicellulose and lignin in the raw wheat straw are not completely degraded, and the intermediate products have not been converted into EL. Longer reaction times are also linked to the hypothesis that EL undergoes further conversion, increasing the residue.

With only a slight decrease in catalytic activity, Guan et al. [13] observed the excellent reusability of the [SO₃Hbmim][HSO₄] IL after five runs. Chen and Long [15] observed the same. They studied the decomposition of all components of sugarcane bagasse with the eco-friendly solvent of ethanol/H₂O using [SO₃Hbmim][HSO₄] catalyst. The authors intensively studied reaction condition parameters such as catalyst dosage, temperature, time and solvent. Under mild conditions of 200 °C for 30 min with [SO₃Hbmim][HSO₄] catalyst, 97.5% bagasse was converted with 66.46% of volatile product yield. According to the results of product analyses using GC–MS, GPC and FTIR, both carbohydrate and lignin were simultaneously degraded.

26% of bagasse was liquefied in the absence of acid IL, compared with much higher values found with liquefaction in the presence of an acid IL. The authors conclude that the acidic nature of the IL catalyst is crucial for bagasse liquefaction.

In the various studies by Amarasekara and co-workers, this was also observed. The authors found that the $-SO_3H$ group functionalized BAILs were more effective in developing catalysis methods for processing cellulosic biomass. These studies revealed that such ILs have a more significant effect on the cellulose depolymerization catalysts than pyridinium and triethanol ammonium cation BAILs.

The authors used the same cations but with the $[Cl]$ anion [1-(1-propylsulfonic)-3-methylimidazolium chloride ($[SO_3Hpmim][Cl]$) and 1-(1-butylsulfonic)-3-methylimidazolium chloride ($[SO_3Hbmim][Cl]$)] as BAILs and acetone as the reaction medium, since renewable acetone can be produced by the acetone–butanol–ethanol (ABE) fermentation process, meaning all the carbon in the final product comes from renewable resources. However, other solvents were selected by this research group, namely ethylene glycol, being the first use of ethylene glycol as a reaction medium ever reported in the liquefaction of cellulose. These reaction mediums (ethylene glycol [3] and acetone [16]) have been proven to lead to greater yields of cellulose depolymerization products as well as cross-reactions of these products with the solvent. In the work of Amarasekara and Wiredu [3], $[SO_3Hpmim][Cl]$ and $[SO_3Hbmim][Cl]$ were used as catalysts in the liquefaction of cellulose in ethylene glycol at 180 °C. These conditions led to a simple mixture. Three products: 2-hydroxyethyl levulinate, 2-hydroxyethyl levulinate ethylene ketal and 2,3,6,7-tetrahydrocyclopenta[1,4]dioxin-5-one, in a ratio of 47:22:31 (mol %), were identified. Detected for the first time in a cellulose liquefaction process, the authors isolated 2,3,6,7-tetrahydro-cyclopenta[1,4]dioxin-5-one as a new C-6 carbohydrate derived cyclopentenone derivative.

Amarasekara and Deng [16] have tested other types of biomass, untreated switchgrass in acetone, to produce hydrophobic liquefied oils. These catalysts converted 39.5% and 31.75% of switchgrass at 120 °C after 3.5 h. The highest biomass conversions were obtained by Amarasekara and Reys [17] in their work with corn cobs and switchgrass. With an increase in the reactional time from 3.5 h to 5 h, the authors obtain conversions of 63.4 ± 0.9 and $56.4 \pm 0.9\%$ (w/w), respectively, with the same catalysts. The highest yield was observed for corn cobs, which has a higher hemicellulose content, suggesting that this component is easily liquefied under the set conditions.

The liquefied products, fractionated by solvent extractions to polar and non-polar fractions, presented a weight proportion of 2:1 for all liquefied bio-oils. In this case, 16 and 19 products were present in the polar and methylene chloride soluble non-polar fractions, respectively. With the comparable liquefaction yields obtained with the two catalysts, the authors concluded that the structural effect of one methylene group in the catalyst was not significant, being the highest biomass conversion yield achieved with $[SO_3Hpmim][Cl]$ catalyst. However, the effect of catalyst loading (from 0.121 to 0.485 mmol) on the BAIL catalyzed liquefaction of corn cobs was found to be very significant, showing conversion percentages $>60\%$.

Using $[bmim][Cl]$ to liquefy two widely used biomass feedstocks, oil palm frond (OPF) and bamboo, Tai and co-workers [18] compared the reaction behaviors of OPF and bamboo in $[bmim][Cl]$ at different treatment times to find the best conditions to overcome the difficulties in hydrolyzing and converting into other products due to the tight and strong hydrogen bonding between the lignin and polysaccharides. The two types of biomass were heated at 120 °C for 2–24 h under atmospheric pressure, obtaining two fractions: $[bmim][Cl]$ -soluble and -nonsoluble. With the characterization of each fraction, the authors found that due to its compact cell wall structure and its less complex nature, the dissolution of OPF in $[bmim][Cl]$ was higher when compared to bamboo. As a result, the decomposition of the crystalline structure of cellulose of OPF was faster, allowing for the $[bmim][Cl]$ to enter its interior. Such effect would facilitate the breakdown of the hydrogen bonding network and consequently the higher solubilization of holocelluloses and lignin and the formation of higher quantities of mono-sugars after 2 h of $[bmim][Cl]$ treatment.

A complete analysis with this IL was performed by Zainol et al. [19] using response surface methodology to optimize the processing conditions for the liquefaction of oil

palm empty fruit bunch (EFB) using [bmim][Cl], considering as independent variables: temperature, time and ratio (IL/EFB). By analyzing the contour plots of liquified EFB yield versus (a) reaction temperature and IL/EFB ratio (b) reaction temperature and reaction time (c) IL/EFB ratio and reaction time, the authors found that there was less interaction between the temperature and ratio on yields of liquified EFB, but that temperature had a significant effect. The optimum conditions for the predicted liquified EFB yield of 80.97 wt.% were obtained with a temperature of 151.9 °C, ratio (IL to EFB) of 4.27 and a reaction time of 112.78 min.

In the work of Cheng et al. [20], [bmim][HSO₄] was used as a catalyst in a biomass fractionation process, carried out with various aqueous alcohol solutions to fractionate coir and poplar into cellulose materials with a lignin content as low as 0.95% and lignin with a delignification rate of up to 98%. The authors found that the catalyst [bmim][HSO₄] exhibited a high enhancement to the lignin extraction with a nearly six-fold increase. Compared with the conventional organosolv lignin, the extracted lignin possessed comparable molecular and thermal stability. In addition, the chemical structure was very similar to milled wood lignin. To investigate the effect of solubility parameters and chemical structure (chain length, hydroxyl position and effect of hydroxyl number of alcohol) and influence of the solvent on delignification efficiency, several alcohols with different boiling points were employed as solvents (ethanol, ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butylene glycol and glycerol). The increase in the carbon chain length led to an increase in lignin extraction efficiency for the alcohols with hydroxyls located in the 1 and 2 or 1 and 3 positions. These hydroxyl positions also played an effective role in biomass processing efficiency. The efficiency sequence for dihydric alcohols with different hydroxyl positions obtained was: 1 and 4 > 1 and 2 > 1 and 3. 1,4-butylene glycol system produced the highest delignification and comparative (or even lower) mass loss of biomass, being considered by the authors the most efficient solvent. Continuing to study the lignin extraction and hemicellulose conversion obtained via fractionation and partial conversion of coir, in the work of Cheng et al. [21], an aqueous 1,4-butanediol/acidic ionic-liquids system was used. With a high relative crystallinity (up to 65%), cellulose-rich materials with a purity of up to 87% were obtained. The authors obtained a delignification of 88% (lower than previous studies) and near-complete conversion of hemicellulose.

The authors also found that the conversion products could be readily extracted from the reaction liquid using ethyl acetate. This was also observed by Ouyang and co-workers [22], who also studied the lignocellulose fractionation of coir with an aqueous glycerol/acidic ionic liquid (AGAIL) system with the same catalyst [bmim][HSO₄], under atmospheric and autogenerated pressure. The process under autogenerated pressure presented higher delignification efficiency and more effective lignocellulose conversion capability than under atmospheric pressure. Under autogenerated pressure, the authors found that 57.7% of the original lignin and 94.2% of the original hemicellulose could be removed, and 68.3% of the original cellulose remained in the cellulose-rich material (CRM). Good recyclability was observed with no significant loss of the catalytic activity, even after five runs.

No studies presented ILs performance after five runs, being this one key factor to be addressed. In Table 3, a resume of mentioned liquefaction studies for herbaceous and agricultural biomass is presented. As seen previously, the most studied ILs are based on [SO₃Hpmim] or [SO₃Hbmim] cations and [Cl] anion. Once again, little comparisons can be made due to the lack of information. Despite this, reaction times were superior to those presented for the previous type of biomass, and yields are inferior, probably due to inferior contents. The high dispersion in how liquefaction yields are addressed makes it almost impossible to compare ILs performance due to the missing information about residue weights which allows the liquefaction yield calculus.

Table 3. Ideal conditions (Type of IL; ILs dosage; solvent(s); temperature (T); reaction time (Rt)) presented by different studies on the usage of ILs as catalysts or solvents on different types of biomass liquefaction. (^a Cellulose rich material yield (%) related to the mass of original biomass used ^b Lignin yield (%) related to the mass of original biomass used ^c Volatile product yield).

Type of Biomass	IL	ILs Dosage	Solvent(s)	Conditions		Yield wt. %	Ref.
				T/°C	Rt/h		
Wheat straw	[SO ₃ Hbmim][HSO ₄]	1.3 g	ethanol	200	1 h	85.5	[13]
Wheat straw	[bmim][Cl]	4 g	sub-critical water	320	0.5 h	86.6	[14]
Sugarcane bagasse	[SO ₃ Hbmim][HSO ₄]	1.5 mmol	ethanol + water (7:3 v/v)	200	0.5 h	66.5 ^c	[15]
Cotton linters	[SO ₃ Hpmim][Cl]	0.2 mmol	ethylene glycol	180	20 h	34.4	[3]
	[SO ₃ Hbmim][Cl]	0.2 mmol				30.5	
Switchgrass	[SO ₃ Hpmim][Cl]	150 mg	acetone	120	3.5 h	39.5	[16]
	[SO ₃ Hbmim][Cl]					31.8	
Corn cobs	[SO ₃ Hpmim][Cl]	0.485 mmol	acetone	120	5 h	63.4	[17]
	[SO ₃ Hbmim][Cl]					62.6	
Switchgrass	[SO ₃ Hpmim][Cl]					56.4	
	[SO ₃ Hbmim][Cl]					53.6	
Oil palm frond	[bmim][Cl]	9 g	-	120	2 h	-	[18]
Oil palm EFB	[bmim][Cl]	4.27 (IL):1 (EFB)	-	151.9	112.8 h	81	[19]
Coir	[bmim][HSO ₄]	1 g	1,4-butylene glycol + water (4:1 v/v)	200	0.5 h	44.6 ^a	[20]
			1,4-butanediol + water (4:1 v/v)			24.1 ^b	
			glycerol + water (4:1 v/v)			39.9 ^a	
					1 h	24.9 ^b	[21]
						~45 ^a	[22]
						~5 ^b	[22]

2.3. Contaminated Biomass and Industrial Biomass Wastes (Semi-Biomass)

Contaminated biomass and industrial biomass wastes represent one of the most complicated types of biomass due to some heterogeneity and diversity among the several sub-groups that it comprises. One of the most popular types is municipal solid waste (MSW), which is produced in higher amount worldwide.

To convert the organic biodegradable fraction of MSW, Sreenviasan et al. [23] studied the effect of anion substitution of BAILs in catalytic thermal liquefaction (CTL). The MSW studied was majorly composed of garden waste, kitchen waste, vegetable waste, papers and cardboard. The objective of this work was to convert this type of waste into carbon densified liquid (CTL-Oil) to be used in several energy and fuel applications due to its carbon content of 48–55% and calorific value of 20–23 MJ/kg. Some ILs were tested, keeping the cation part, [benz-SO₃Him]⁺ and changing the anion: [H₂PO₄]⁻; [HSO₄]⁻; [TsO]⁻ and [TfO]⁻. The use of [HSO₄]⁻ showed a high effect in the CTL process resulting in >85% MSW conversion and >80% CTL-Oil production without gas or char. These BAILs assisted the ease of dissolution and hydrolysis of biomass in producing CTL-Oil via hydrolysis, condensation, cyclisation and dehydration reactions. However, several major parameters affect hydrothermal liquefaction processes, and these authors investigated some. The results (Table 4) showed that, for example for the reaction temperature parameter, for the experiments conducted between 60 °C to 150 °C, the maximum and minimum CTL-Oil yield obtained was >80% at 120 °C and <30% at 60 °C, respectively. The authors also attributed incomplete conversions to lower temperatures (<120 °C) and further degradation of the organic phase products to a higher temperature (>120 °C), such as other authors.

Reaction time and BAILs concentration were also parameters addressed in this study. The CTL reactions were conducted at different time intervals (0.5–2.5 h). The optimal conversion was obtained with 1.5 h. Beyond this value, the authors refer to the possibility of further polymerization of CTL-Oil components, resulting in water-soluble products. As for the BAILs concentration, CTL was conducted at different concentrations of BAIL from 10 to 45 mmoles (w.r.t. dry wt. of feedstock). Once again, CTL-Oil yield increased until a certain value, decreasing with a catalyst concentration above 25 mmoles. The authors found the same explanation for this fact; excessive catalyst loading promotes the formation of water-soluble products through further reactions with liquefied components of MSW.

Table 4. Ideal conditions {Type of IL; ILs dosage; solvent(s); temperature (T); reaction time (Rt)} on the usage of IL as catalysts for municipal solid waste liquefaction.

IL	ILs Dosage	Solvent(s)	Conditions		Yield wt.%	Ref.
			T/°C	Rt/h		
[BenzSO ₃ Him][HSO ₄]	25 mmol	-	120	1.5 h	>80 ^a	[23]

^a CT-OIL yield.

3. Final Remarks

The effectiveness of acidic ionic liquids as catalysts in biomass liquefaction has proved to be advantageous in some liquefaction processes. There are several factors that, in general, can improve liquefaction yield, such as raising the temperature, raising pressure, prolonging the reaction time or increasing the catalyst dosage. However, this relationship is not linear for all factors. Authors found that sometimes there is an ideal value beyond which this yield does not change significantly or even diminishes. This is why studies focusing on different factors are essential to understand the behavior of a given IL in biomass liquefaction. The studies mentioned above often lack crucial information that would be important for comparing the type of IL and dosage in the liquefaction of certain types of biomass. Examples such as information about IL purity, how the catalyst dosage was calculated (upon biomass weight or biomass + solvent weight) are the most important ones that should be addressed in future research regarding this subject. The amount from which an IL is considered a solvent and not a catalyst is not addressed, being also a crucial issue.

As for the selection of the right IL for the job, this is not easy. With several possible combinations, the role of both cation and anion is not conclusively defined. Despite the evidence that the anion plays the more decisive part in the liquefaction yield, ILs with cations possessing acid sites and anions with this characteristic was found to contribute to a liquefaction yield similar to that obtained with H₂SO₄. Such effects were attributed to the presence of double acid sites, for example, in [SO₃Hbmim][HSO₄] and [SO₃Hpmim][HSO₄]. Evidence also showed that a better yield could be, in fact, obtained with [HSO₄] anion. This would require more studies using the same type of biomass, and IL catalysts with different anions and cations within the same dosage for establishing the role of both anion and cation in this process. Such work would also allow retrieving valuable information about the influence of the type of ionic liquid on the chemical compositions of liquefaction products.

Apart from the influence of IL in the liquefaction process, solvents are also crucial. The increase in the carbon chain length of the solvent appears to lead to an increase in lignin extraction efficiency. However, this efficiency seems to be linked to the hydroxyl positions in the carbon chain. This justifies the need for studies that include the influence of both IL and solvent in biomass liquefaction.

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Abbreviations

IL	Ionic Liquid
PEG400	polyethylene glycol 400
AIL	Acidic Ionic Liquid
BAIL	Brønsted acidic ionic liquids
FTIR	fourier-transform infrared
MCC	microcrystalline cellulose
DP	degree of polymerisation
EL	ethyl levulinate
GC-MS	gas chromatography–mass spectrometry
GPC	gel permeation chromatography
ABE	acetone–butanol–ethanol
EFB	empty fruit bunch
CRM	cellulose-rich material
2-HAF	2-hydroxyacetylfuran
MSW	municipal solid waste
CTL	catalytic thermo liquefaction
CTL-Oil	carbon densified liquid

Ionic Liquid Acronym

[mim][HSO ₄]	1-methylimidazolium hydrogensulfate
[bmim][HSO ₄]	1-butyl-3-methylimidazolium hydrogensulfate
[SO ₃ Hpmim][HSO ₄]	1-(3-sulfopropyl)-3-methylimidazolium hydrogensulfate
[SO ₃ Hbmim][HSO ₄]	1-(4-sulfobutyl)-3-methylimidazolium hydrogensulfate
[bmim][CH ₃ COO]	1-butyl-3-methylimidazolium acetate
[bmim][Cl/AlCl ₃]	1-butyl-3-methylimidazolium chloride-aluminum chloride
[emim][Cl/AlCl ₃]	1-ethyl-3-methylimidazolium chloride-aluminum chloride
[amim][Cl/AlCl ₃]	1-allyl-3-methylimidazolium chloride-aluminum chloride
[bmim][Cl]	1-butyl-3-methylimidazolium chloride
[bmim][Cl/NiCl ₂]	1-butyl-3-methylimidazolium chloride-nickel chloride
[bmim][Br]	1-butyl-3-methylimidazolium bromide
[emim][Cl]	1-ethyl-3-methylimidazolium chloride
[bmim][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
[bmim][Br/NiCl ₂]	1-butyl-3-methylimidazolium tetrafluoroborate-nickel chloride
[py][Cl]	pyridinium chloride
[mim][Cl]	1-methylimidazolium chloride
[emim][CH ₃ COO]	1-ethyl-3-methylimidazolium acetate
[emim][HSO ₄]	1-ethyl-3-methylimidazolium hydrogensulfate
[SO ₃ Hpmim][Cl]	1-(1-proylsulfonic)-3-methylimidazolium chloride
[SO ₃ Hbmim][Cl]	1-(1-butylsulfonic)-3-methylimidazolium chloride

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