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Recent Development of Biomass Conversion using Ionic Liquid-based Processes

Megawati Zunita *
Risha Diah Rhamadhani
Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Bandung, Jalan Ganesha 10, Bandung, West Java, Indonesia, 40132
**e-mail:* m.zunita@che.itb.ac.id

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Abstract. The amount of biomass products generated globally increases year after year. Nature produces lignocellulose, which is largely constituted of three components in the following order: cellulose (34–50%), hemicellulose (15–35%), and lignin (5–30%). A promising conversion method known as biomass conversion employs a liquid media-based process to address the issue of an abundance of biomass as waste. Converting biomass with ionic liquid (IL) can address not only environmental issues caused by the abundance of biomass waste but also generate new energy sources or new products with economical selling value. IL can be employed as a green catalyst, solvent, or electrolyte, as well as in a number of conversion processes. In general, 1-alkyl-3-methyl-imidazolium-based cations are the most commonly used IL types for biomass conversion. The conversion conditions are relatively mild, consisting of a low temperature of around 95-220 °C, 1 atm, for 10–240 minutes. This paper review is expected to be a significant reference in the future for the development of other biomass conversion processes.

Keywords: Biomass Conversion, Development Process, Ionic Liquid

INTRODUCTION

One irrefutable reality is that fossil fuels, including natural gas, oil, and coal, are still the primary means of meeting global energy consumption demand. However, science has proven that fossil fuels have many disadvantages, such as being non-recyclable and not environmentally friendly. The energy demand is never balanced between energy consumption and available fossil fuels every year. In 2020, the global energy demand from fossil fuels was recorded at 81.3 Btu and was expected to increase about 7% in 2022. If the demand keeps increasing each year, then fossil fuels are only enough for 50 years (Zhang et al., 2014). The current problem is not only the shrinkage of fossil fuels but also the abundant emissions (such as fly ash particulate and hazardous gases), which are produced from the conventional fossil fuel combustion process. The greenhouse gases that are released into the atmosphere, such as nitrogen oxide, carbon dioxide, and sulphur oxide, may become the primary cause of global climate change. Both issues then push the desire to develop alternative fuels from non-fossil sources.

Biomass is one of the world's largest resources for fulfilling human wellbeing demands. Compared to other renewable energy sources such as nuclear, wind, hydroelectric,

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solar, and geothermal power, biomass has led the current research and development trend in the search for renewable energy sources to support the deduction of fossil fuels (M. Li et al., 2017).

The biomass source is abundant and includes all kinds of organic matter, plant-based materials and is naturally available worldwide (Xu et al., 2016). The amount of biomass each year is estimated to be 170 billion metric tonnes, with carbohydrates accounting for 75% of this total, but humans consume only 3-4% of these compounds for food and non-food purposes(Xu et al., 2016). Biomass production was recorded as eight times greater than the total annual global consumption, placing it fourth below the fossil fuel sources of oil, coal, and natural gas. This trend also affected the demand for biomass sources, which was predicted to be around 10 million to 30 million tonnes by 2030 (Chinnappan et al., 2016). According to the Imperial College Centre for Energy Policy and Technology, the obtainable biologically productive agricultural area is approximately 13 Gha, with approximately 1.5 Gha used to expand arable crops and 4 Gha inhabited by forests. Therefore, 5.5 Gha of land has the capacity to offer biomass feedstock. Biomass which can be converted into new products, must contain intrinsic chemical energy (Chinnappan et al., 2016).

Some kinds of biomass can be used, such as forest biomass, industrial waste, energy crops, and agricultural by-products (Lynam et al., 2012). Although it has been established that biomass resources are abundant and environmentally friendly, their usage presents new challenges, notably in the area of energy generation. In this case, the difference in energy density between fossil fuels and biomass is the main factor. Biomass materials have lower energy density than fossil fuels, so biomass materials produce lower thermal efficiency. This low energy content is due to the low bulk density, high moisture content, and high oxygen content in the raw feedstock, limiting the direct combustion process (Bajwa et al., 2018). Today, people have a high desire to develop green chemistry in converting biomass waste into new products.

Nowadays, researchers and industry place a high value on converting biomass resources into renewable energy sources through environmentally friendly media, a process known as the green process. One of the novels and promising media that has become a trend lately is ionic liquids (ILs). Researchers chose ILs because of their excellent thermal stability, wide electrochemical window, virtually zero vapor pressure, and tuneable features in terms of polarity, hydrophobicity, and solvent miscibility behavior with appropriate modifications to their cations and anions (Zhang et al., 2014; M. Li et al., 2017; Khan et al., 2019; Xu et al., 2016). Because of the unique properties of the ILs, they have been broadly applied in various fields beyond separation, catalysis, photoelectric transformation, and material synthesis. Numerous papers related to biomass conversion in ionic liquid were discovered in the Scopus database, as shown in Fig. 1, leading us to conclude that this field will gain greater interest over time, ushering in a new era of biomass conversion.

Research findings in biomass conversion have already shown that ILs perform better than other conventional organic solvents available. As shown in Fig.2, certain uses of biomass conversion products utilizing ILs solvent have been described.

This year, the exploration of ILs has emerged as a significant and exciting research topic among scientists. This paper review article compares and contrasts them. This study aimed to give further references and significant points of view on biomass conversion and the role of ILs in academia and industry. The next sections of this paper give a more in-depth analysis.

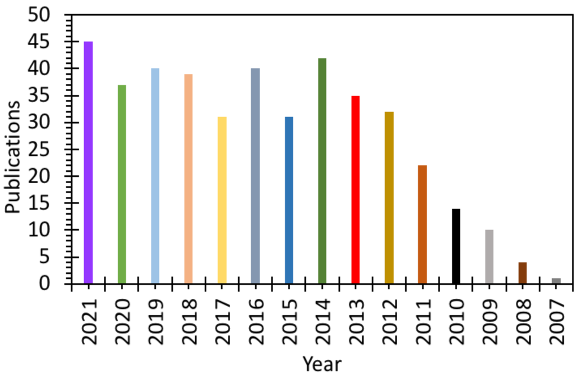

Fig. 1: Annual Number of Publication on Biomass Conversion by Ionic-Liquid Method until November 16, 2021; The Search was Conducted from The Data from Scopus with TITLE-ABS-KEY (biomass conversion in ionic liquid)

BIOMASS MATERIAL AS A RESOURCE

According to the definition, biomass is an organic substance derived from plants or animals. Biomass, which is made up of chemical energy obtained from the sun, has become a source of renewable resources in today's world. There are two main ways to prepare biomass-based energy; firstly, by burning the biomass to produce heat, and secondly, by converting the biomass into renewable liquid and gaseous fuels through various processes (IEA,2020). The production of renewable energy from biomass will surely help reduce the overall world's need for fossil fuel resources. Various biomass products contain energy content, i.e. terpenes, lignin, cellulose, sugars, and vegetable oils (Hartanto et al., 2017). Terpenes have the largest energy content in the sequence, but they have low productivity, which is one of the conditions in the manufacture of biofuels.

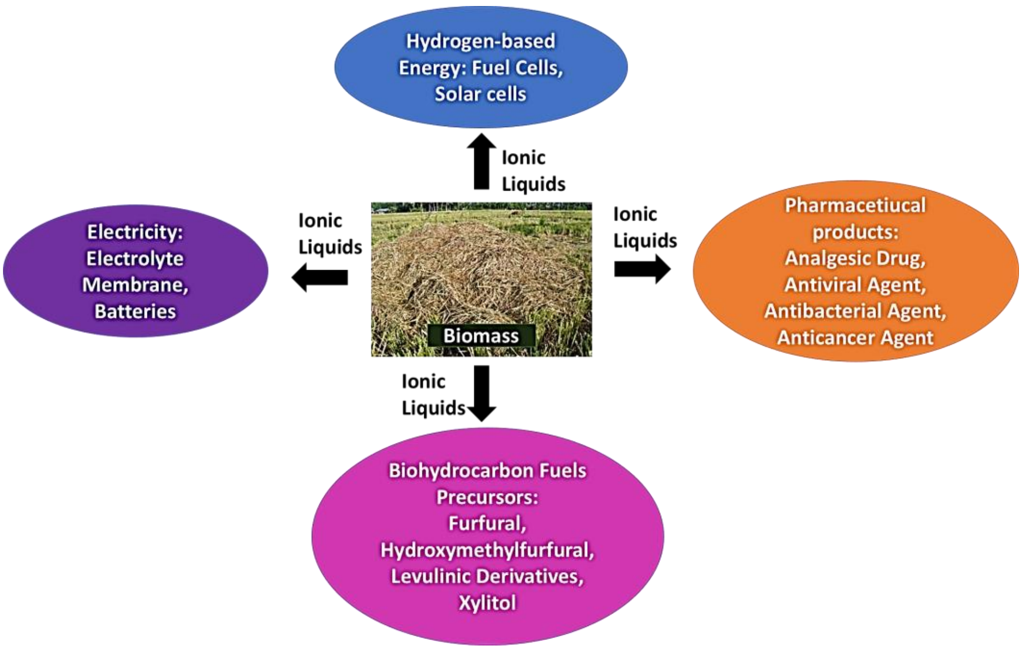

Fig. 2: Various Applications of Biomass Conversion Products from ILs Pretreatment

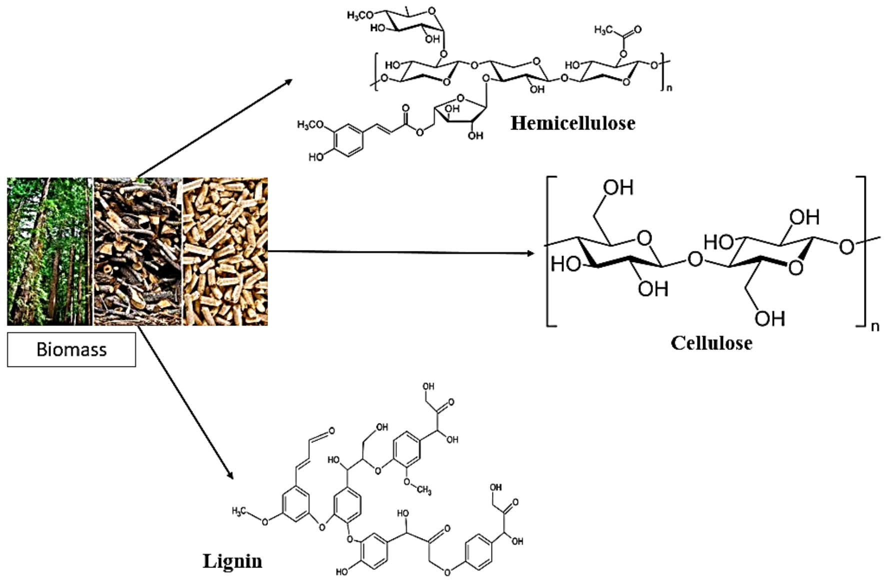

Fig. 3: Content of Biomass Components, adopted from ref. (Xu et al., 2016)

Furthermore, vegetable oils are becoming the next biomass product that could become a potential renewable energy source. The fatty acid in vegetable oils is widely used as sustainable feedstock in some chemical processing industries. However, the production of fatty acids and oleochemicals is prohibited by the volume of oils needed for uneatable use. This limited availability of oils has shown the researchers to use lignocellulosic biomass as a source of renewable energy and chemical feedstock. The primary idea behind biomass conversion is to utilize less hazardous chemicals, enhance the profitability of biorefinery products, and reduce environmental pollution.

Lignocellulosic biomass has become the most relevant biomass component for inquiry in biomass conversion due to the quantity of feedstock worldwide. Lignocellulose is produced by nature. It mainly consists of three components in order; cellulose (34-50%), hemicellulose (15-35%), and lignin (5-30%) (Xu et al., 2016), as shown in Fig.3. All components were linked to each other by covalent and hydrogen bonds.

Cellulose has become the most widely used ingredient of lignocellulosic biomass because of its promising aspects as a substitute feedstock for the production of biofuel and biochemicals. Cellulose is a homopolymer structure containing glucopyranose repeating units connected by β-(1-4) glycosidic bonds. Cellulose chains are arranged as parallel and long chains interlocked through H-bonding and van der Waal forces. The challenge of lignocellulosic conversion is due to the close packing of chains and three-dimensional crystalline structure (Hasanov et al., 2020). The three-dimensional structure contains hydrogen bonding, a high degree of crystallinity, and polymerization, which restrict cellulose's hydrolysis/conversion process into glucose and even other chemicals.

Table 1. Various Biomass Sources are Frequently Converted Through IL-Based Processes

Years	Biomass Type	Biomass Origin	IL Type	Ref.
2012	Rice Hulls	Agriculture waste	[EMIM][Ac], [AMIM] Cl	(Lynam et al., 2012)
2013	Wood Bark	Forest	[BMIM]Cl	(Ilpeläinen et al., 2007)
2012	Cassava pulp	Agriculture waste	[EMIM][AC], [EMIM][DEPO$_4$]	(Weerachanchai et al., 2012)
2020	Sugars	Agricultural Waste	[EMIM]Cl	(Ofrasio et al., 2020)
2017	Rubber Wood	Plantation	[BMIM]Cl, [BMIM][Ac]	(Khan et al., 2016)
	Bamboo	Plantation	[EMIM][Gly], [EMIM][TFA]	(Muhammad et al., 2011)
2007	Corn Stalk	Agricultural Waste	[SBMIM][H_2SO_4], [BMIM][H_2SO_4]	(C. Li & Zhao, 2008)
2010	Pine Wood	Forest	[SBMIM][H_2SO_4], [BMIM][H_2SO_4]	(Brandt et al., 2010)
2007	Bagasse	Industrial Waste	[SBMIM][H_2SO_4], [BMIM][H_2SO_4]	(C. Li & Zhao, 2008)
2011	Cotton-waste	Textile Industry	[AMIM]Cl	(Hong et al., 2012)

The main focus of the biomass conversion system is to understand the analysis of the structure and chemical compounds of various biomass feedstocks. Those parameters directly influence the overall yield of the chemical product converted by biomass. As it has a complex structure and strong interaction between all the constituents of cellulosic biomass, it is important to break down the chemical and physical bond first before converting the biomass. Table 1 shows the types of biomass that can be processed into biofuels and biochemicals, along with the types of IL used in the conversion process.

The ultimate challenge of biomass conversion was due to the complex structure and the strong interaction between all the lignocellulosic materials. Four main chemical bonds were available in lignocellulosic materials, i.e. ester, C-C, hydrogen, and ether bond. These bonds connected the individual components (linkage between polymers) and the different constituencies (interpolymer linkage of biomass). The complexity of biomass structural entanglement becomes the cause of difficulties in converting biomass into platform chemicals or even fuels. Thus, researchers have been considering adding a pretreatment method to this conversion to facilitate the conversion of lignocellulosic biomass into platform chemicals. In the next session, the conventional technique of biomass conversion will be discussed before the IL-based processing approach is described.

BIOMASS CONVERSION USING CONVENTIONAL METHODS

Researchers have been converting biomass into biofuel and biochemicals using conventional methods before the first publication about converting biomass using ILs was published. Generally, three conventional methods are mostly used in biomass conversion; thermochemical conversion, direct combustion, physio-chemical conversion, and biological conversion (Zunita et al., 2020; Ruya et al., 2020). Each method is mostly used to produce biofuels and biochemicals.

The thermochemical conversion process is the most basic and earliest method of biomass conversion. Pyrolysis, gasification, liquefaction, and combustion are used in the thermochemical conversion process. Direct combustion is the most basic approach. Biomass was converted into heat using this method of burning. All types of biomass are burned directly to generate heat, then utilized to power steam turbines and generate electricity.

The negative of this combustion process is the emission, which is CO_2 and CO (similar to fossil fuel combustion), and the biomass needs to be dried up first before combustion to get maximum yield and efficiency. The emissions from this process are the world's biggest concern since they will affect the overall environmental system. The emissions from this process have become the reason people are looking for another greener method. The next method is thermochemical biomass conversion.

This thermochemical conversion of biomass occurs via gasification, pyrolysis, liquefaction and combustion (Duun et al., 2012). Pyrolysis and gasification are thermal decomposition processes that use biomass as feedstock material, heated in closely pressurized vessels at high temperatures (around 400-500 °C). These two processes can produce biofuels such as bio-oil, biofuel for jet machines and biodiesel.

The next common method is the biochemical method. This biomass conversion method includes two processes, which are anaerobic digestion and fermentation (Naqi et al., 2018). The anaerobic digestion method converts the biomass material directly into biogas and biofertilizer. Meanwhile, the fermentation process produces biochemical products such as bioethanol by adding microorganisms (mostly yeast).

This fermentation process faces a waste problem after the product is obtained. Mostly, even though this waste can be used for other functions, the amount of waste is too much to be handled. Although the fermentation method is simple, it cannot be employed in large-scale biochemical production since it requires massive crops.

There is also one biomass conversion method called microwave irradiation. This method is known to produce high-yield biofuel products from biomass waste (Bundhoo, 2018). Some studies have reported the use of MW irradiation for biomass pretreatment. Microwave irradiation works when waves from the electromagnetic spectrum range from 0.3 to 300 GHz. When these microwaves transmit, the waves are transformed into specific frequencies, causing the biomass material to heat up and absorb the waste's energy (Puligundla et al., 2016).

Table 2. A Comparison of Various Conventional Methods for Biomass Conversion

Method	Process	Product	Condition	Yield	Ref.
Direct combustion	Convert biomass into heat	Heat to generate electricity	T = maximum around 740-1300 ºC	Power and heat	(Adams et al., 2018)
Gasification	Convert organic feedstock into gaseous component	Syngas	T = moderate to high (600 – 1200 ºC), small particle is preferable	Gas yield(m^3/kg of biomass)	(Adams et al., 2018)
Hydrothermal Liquefaction	Convert aqueous biomass slurries with high moisture content	Bio-oil, chemicals	T= 400-1200 ºC, high pressure	Bio oil: 60-75%	(Adams et al., 2018)
Biological conversion	Anaerobic digestion and fermentation	Ethanol	Fermentation of biomass by adding yeast	Ethanol: 85%	(Adams et al., 2018); (Naqi, 2018)
Microwave	Irradiating biomass by using microwave irradiation	Biofuels	T = 333 K; Time: 30 min	91,4 % mol of biofuel	(Bundhoo, 2018)
Pyrolysis	Thermal decomposition of biomass with the absence of oxygen	Liquid bio-oil, chemical feedstock	P at atmospheric, T around 400 -550 ºC	Liquid bio oil: 65-75%; Chemical feedstock solid form: 13-25%	(Adams et al., 2018); (Ren et al., 2020)
Extraction	Transesterification process	Biodiesel	Batch reactor T = 298-338 K	FAME (biodiesel) 97.7%	(Boz et al., 2009)

GENERAL IONIC LIQUIDS ARE USED IN BIOMASS CONVERSION

In 2002, the application of ILs as cellulose dissolvers was first described (Swatloski et al., 2002). The first publication gained researchers interest in this new field. For the last decades, the exploration of this IL usage has grown rapidly among researchers, as ILs can perform as green solvents to reduce the dependency on toxic and harmful solvents such as organic solvents or chlorinated solvents (Wikes et al., 2003; Jasstorf et al., 2003; Zunita et al., 2020; Zunita et al., 2021). ILs have been explored due to their advantages, such as the high selectivity of impurities in liquid form (Xu et al., 2016). In general, ILs are liquid salts with temperatures under or close to room temperature. The chemical and physical characteristics of ILs can be altered by modifying the cation and anion combinations. (Brandt et al., 2010). Modern ILs mostly consist of organic cations in the form of aliphatic ammonium ions, quartered aromatics, sulfonium, and alkylated phosphonium (Brandt et al., 2011; Zunita et al., 2021). Therefore, ILs are classified as organic or inorganic salts based on the cations and anions that contain the organic or inorganic substance. Fig. 4 shows some representative common cations and anions used in biomass conversion.

Several IL types have been discovered to dissolve cellulose, lignin, hemicellulose, and untreated lignin (Zunita et al., 2021; Brandt et al., 2010; Agrella et al., 2018). ILs can dissolve because the anions and cations can break the strong interaction of internal hydrogen of the biomass by providing electron donor or electron acceptor pairs, thus reducing the crystallinity of biomass to facilitate dissolution (Mudhoo et al., 2018). ILs mostly consist of Fig. 4 shows two ILs based on the ion type: anion and cation. Generally, ILs are formulated in the form of bulky 1,3-dialkylimidazolium, alkylammonium, alkylphosphonium, or alkylpyridinium organic cations and inorganic anions such as most frequently $AlCl_4^-$, BF_4^-, or PF_6^- but also NO_3^-, ClO_4^-, $CF_3COO_2^-$, $CF_3SO_3^-$ or CH_3COO^- and other anions. Table 3 demonstrates the features of ILs as well as their application in biomass conversion.

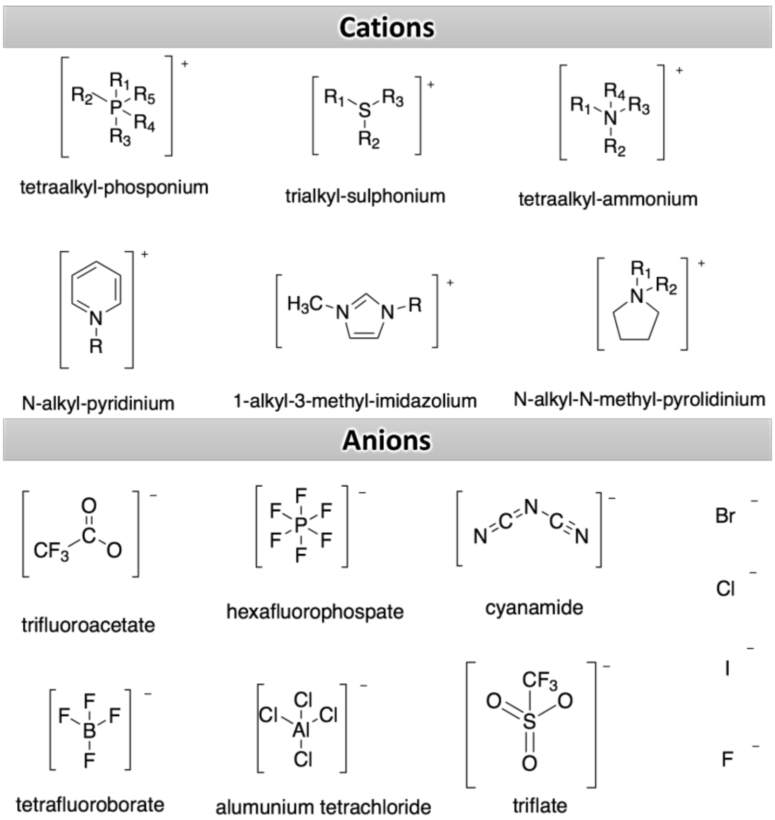

Fig. 4: Some Cations and Anions of ILs are Mostly Used in Biomass Conversion

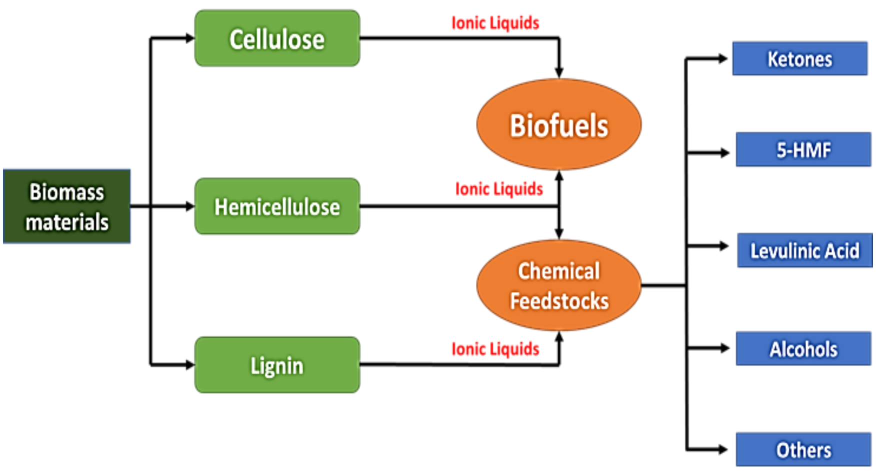

Fig. 1: Potential Products of the Three Major Components of Lignocellulosic Conversion

Table 3. Properties of Some Most Used ILs

IL	Properties	Applications	Ref.
[BMIM]Cl	ρ = 1.081 g/cm^3 Melting point = 65-70 °C Soluble in water and organic solvent	- Glucose Conversion to 5-HMF Solvent for Cellulose conversion to ethanol	(C. Li & Zhao, 2008); (Junnienkul et al., 2018)
[BMIM]Br	ρ = 1.30 g/cm^3 Melting Point = 65 –75 °C Boiling point = 547.5 °C Miscibility in water	Solvent for sucrose conversion to 5-HMF	(Chinnappan et al., 2016); (Kim et al., 2004)
[BMIM][PF$_6$]	ρ = 1.36 g/cm^3 Melting Point = -8 °C Insoluble with water	Solvent for hydrolysis of biomass	(Anderson & Armstrong, n.d.)
[BMIM] [TfO]	ρ = 1.29 g/cm^3 Melting Point = 16 °C Miscibility with water	Solvent to hydrolysis of biomass	(Anderson & Armstrong, n.d.)
[EMIM]Cl	ρ = 1.20 g/cm^3 Melting point = 77-79 °C Boiling point = 484.6 °C	Glucose conversion to 5-HMF	(Chinnappan et al., 2016)
[BMIM][BF$_4$]	ρ = 1.31 g/cm^3 Melting point = -75 °C Miscibility in water	Catalyst for fructose conversion to 5-HMF	(L. Liu et al., 2018)
[OMIM]Cl	ρ = 1.00 g/cm^3 Melting point = 12 °C Slightly soluble in water	Solvent for cellulose conversion to levulinic acid	(L. Liu et al., 2018)

THE ROLE OF IONIC LIQUID IN BIOMASS CONVERSION

Thus far, lignocellulose and derivatives have been converted using ionic liquid to produce HMF, levulinic acid, furfural, formic acid and others, as shown in Fig.5. IL plays a significant role in biomass conversion, particularly as a medium and catalyst. This is assisted by optimal operating parameters (temperature and conversion time) to achieve maximum yield. Because of the high oxygen content in biomass, around 40-45% of the total, some oxygen section needs to be eliminated in the form of CO_2 and H_2O before converting the lignocellulosic biomass into liquid biofuels. The key topics covered in this section include the role of IL in ethanol synthesis, 5-HMF generation, and levulinic acid production from cellulose.

Li reported that corn stalk in a hydrolyzed form diluted in [BMIM] Cl and [BMIM] [H_2SO_4] showed reducing sugar yields of about 68% and 71%, respectively [91]. Then, the author also dissolved wheat straw in the mixture solvent containing [EMIM][OAc], [BMIM]Cl, and numerous phosphoric ILs along with 1-ethyl-3-methyl imidazolium diethyl phosphate ([EMIM][DEP]), 1-ethyl-3-methyl butylpyridinium diethylphosphate ([EMBy][DEP]), and 1-ethyl-3-methyl imidazolium dibutyl phosphate ([EMIM][DBP]), and it was concluded that [EMIM][DEP] resulted out the highest yield of reducing sugars of 50% after 1-hour pretreatment process at 100 °C. However, the use of a high concentration of ILs might interrupt the enzyme productivity during the next fermentation process. To support enzyme productivity, it needs a sufficient amount of water. Furthermore, the conversion process of cellulose to ethanol through the fermentation of sugar is an important pretreatment step for the conversion of biomass into biofuel.

Hydroxymethylfurfural from Cellulose

Hydroxymethylfurfural (5-HMF) is currently popular because it can be converted into building blocks of chemicals that can then be converted into biofuels. It has been done on the hydrogenation, which produces 2,5-dimethylfuran. In addition, the combination of the condensation reaction of 5-HMF and hydrodeoxygenation, which can produce C7–C15 liquid alkanes. ILs work as powerful solvents for the dehydration of monosaccharides to form HMF by breaking the intermolecular hydrogen bonds (Wenten et al., 2019; Zunita et al., 2020). The scheme of HMF production is presented in Fig. 6. The ILs also increase the selectivity and recovery of the conversion process of monosaccharides to HMF.

Although 5-HMF has a versatile application, it has not been fully made on an industrial scale due to the high production costs. Zhang et al., 2014 were the first to report that metal halides in the form of [EMIM] [Cl] are effective catalysts for converting carbohydrates into 5-HMF. Zhang researched the usage effect of plenty of metal halides and a particular number of ILs such as ([BMIM][Cl], [EMIM][Cl], [OMIM][Cl]) on the dehydration reaction of sugars. It is reported that the highest yields for the conversions of fructose and glucose to 5-HMF were 83% and 70%, respectively. Then, Zhao gained a higher yield when conversing glucose into 5-HMF, about 91%, by using combined ILs chromium salt and [BMIM] [Cl] underneath microwave irradiation. Besides 5-HMF cellulose, ILs can produce other profitable chemicals such as sorbitol, glucose esters, and 2-5-DMF, which can be directly used as fuels or chemical precursors.

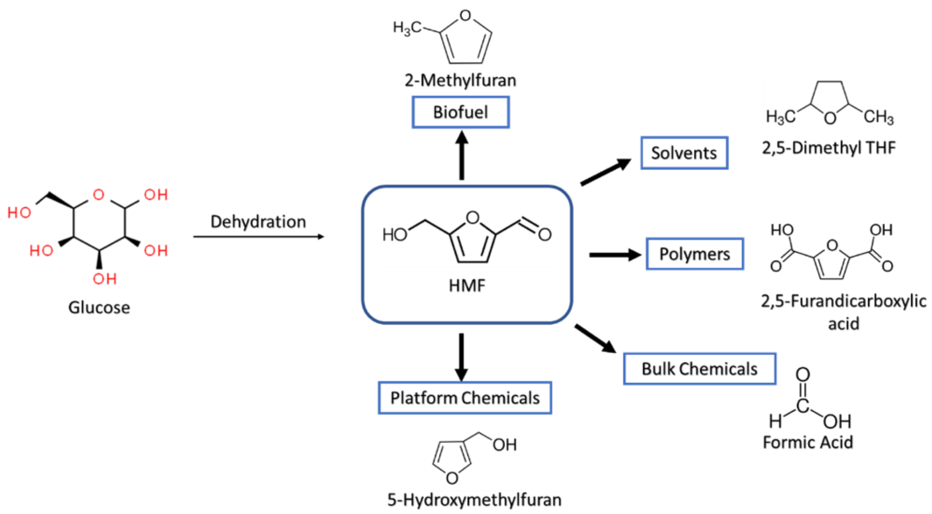

Fig. 6: Scheme of HMF Production from Glucose Conversion

Levulinic Acid from Hydrolisis of Biomass

Lignocellulosic biomass to Levulinic Acid (LA). LA mostly works as a viable chemical bridge between the biomass and petroleum cessing industries. LA can be converted into γ-valeroactone (GVL), and GVL can be further converted into liquid alkenes via a hydrogenation process, which later has potential value as renewable biofuels. LA is not only becoming a promising basic chemical platform for biofuels but also for other industrial applications such as cosmetics, drug delivery, intermediate chemical resins, the pharmaceutical industry, polymers, and so on (Vaniz et al., 1976).

LA can be produced from several different biomass feedstocks, including polysaccharide families such as starch, hemicellulose, cellulose, and chitin. The hydrolysis process of the feedstock can lead to the production of monosaccharides such as fructose and glucose (Shojaeiarani et al., 2019). The scheme of LA production from biomass conversion is presented in Fig. 7.

Some research has been published on the synthesis of LA using ILs sourced from diverse biomass sources (rice straw, pinewood, maize stalk, and bamboo). In 2018, one report demonstrated that rice straw can produce LA through a one-pot reaction of acidic ILs (i.e., $[C_3SO_3HMIM]HSO_4$) as a catalyst.

Those reactions occur for 30 minutes at 180 °C and produce LA with a yield of 21% (Y. Liu et al., 2020). This approach has demonstrated that the interaction between acidic ILs and hydrogen bonding in biomass might lead to a higher yield of LA. The catalyst in this reaction can be recycled up to five times without losing its activity ability. The one-step green conversion of lignocellulosic biomass to LA has paved the way for a promising route in biomass conversion for lignocellulosic feedstocks.

Zunita reported a novel modified IL in 2020 that served as a solvent for producing LA and formic acid (FA). The research focused on a new hydrophobic IL imidazolium-based compound known as 1,3-dipropyl-2-(2-propoxyhenyl)-4,5-diphenylimidazolium iodide ([DPDIM]I). In this reported work, the maximum yield obtained from the IL conversion was 94% LA and 18% FA with the help of H_2SO_4 as catalyst. Zunita also found that in the presence of H_2SO_4, [DPDIM]I perform better as a solvent than water, and that its performance improves over time.

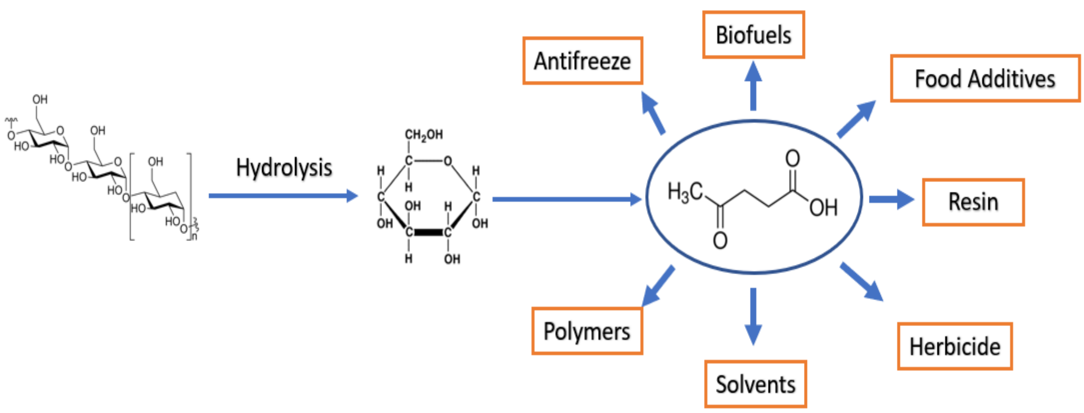

Fig. 7: Basic Scheme on LA Production from Biomass Conversion and Applications

Table 5. An Overview of Reaction Conditions for the Production of Biochemicals Using Ils

Feedstock	ILs	Solvent	Catalyst	Operating Conditions	Yield	Ref.
Sugarcane bagasse	[BMIMSO$_3$H] [HSO$_4$]	H_2O	H_2SO_4	T = 170 °C; Time = 75 min	LA, 55%	(Zhang et al., 2014)
Corn Stalk	[C$_4$(MIM)$_2$] [(2HSO$_4$) (H$_2$SO$_4$)$_4$]	-	-	T = 95 °C; Time = 60 min	LA, 70%	(Zhang et al., 2014)
Sucrose	[EMIM]Br [BMIM]Br [AMIM]Cl	[NMP][HSO$_4$]	H_2SO_4	T = 120 °C; Time = 60 min	5-HMF, 72-80%	(Chinnappan et al., 2016)
Fructose	[CMIM][Cl] [BMIM]OH [BMIM]Cl	DMSO EtOH Amberlyst-15	-	T = 160 °C; Time = 120 min	5-HMF, 92%	(Chinnappan et al., 2016)
Glucose	[BMIM]Cl [AMIM]Cl [BMIM][BF$_4$]	$IrCl_3$ $CrCl_3$	Boric-acid	T = 100 °C; Time = 180 min	5-HMF, 78,8%	(Chinnappan et al., 2016)
Cellulose	[C$_2$MIM][Cl]	H_2O	$CrCl_3$	T = 120 °C;	5-HMF, 10%	(Hou et al., 2017)
Pine Wood	[C$_2$MIM]Cl	H_2O	$CrCl_3$	T = 100 °C; Time = 60 min	5-HMF, 71.6%	(Brandt et al., 2010)
Paddy straw	[C$_3$SO$_3$HMIM][HSO$_4$]	H_2O	HCl	T = 220 °C; Time = 45 min	LA, 24%	(Signoretto et al., 2019)
Bamboo	[C$_4$(MIM)$_2$] [(2HSO$_4$) (H$_2$SO$_4$)$_4$]	H_2O	-	T = 100 °C; Time= 60 min	LA, 47,5%	(Signoretto et al., 2019)
Rice Straw	[C$_3$SO$_3$HMIM] [HSO$_4$]	H_2O	$S_2O_8^{2-}/ZrO_2^-$ $SiO_2^-Sm_2O_3$	T = 180 °C; Time = 10 min	LA, 21 % to 46%	(Signoretto et al., 2019)

The optimum conditions for this cellulose conversion using ILs solvent [DPDIM]I and H_2SO_4 as a catalyst are at a reaction time of 120 min and a temperature of 140 °C. Furthermore, [DPDIM]I can be recycled and reused up to five times (Zunita et al., 2020).

Besides solvents and catalysts, ILs can also be used in the separation process. One of the well-known conventional methods for the separation process is membrane technology (Makertihartha et al., 2017; Zunita, 2021; Zunita et al., 2018). Membrane technology can be combined with ILs to increase the selectivity of the separation process. The method is called the SLM, or supported liquid membrane method (Makertihartha et al., 2017; Zunita et al., 2021; Zunita, 2021).

This combination method works well in a three-phase simultaneous process: extraction from the feed phase to SLM, fluid diffusion through SLM, and re-extraction process in the collected phase. ILs in the SLM can improve the endurance of the membrane technology. Two specific membranes can be easily combined and supported; liquid membrane and hollow fiber (Makertihartha et al., 2017; Makertihartha et al., 2017 ; Zunita et al., 2018).

Table 6. Comparison of Various ILs on Biomass Conversion Product Yield

ILs	Biomass	T(°C)	Time(min)	Yield	Ref.
[BMIM]Cl	Cellulose (bagasse)	100	60	Reducing sugar for Ethanol, 68%	(Zhang et al., 2014)
[BMIM]Cl-H_2O	Cellulose (Penicillium janthinellum)	100	60	Reducing sugar for ethanol, 70%	(Zhang et al., 2014)
[BMIM]Cl	Sugar	120	30	HMF, 70-83%	(Brandt et al., 2011)
[EMIM]Cl	Sugar	120	30	HMF, 70%	(Brandt et al., 2011)
[OMIM]Cl	Sugar	120	30	HMF, 70%	(Brandt et al., 2011)
[C_3SO_3HMIM]H_2PO_4	Cellulose	170	300	LA; 16.7%	(Khan et al., 2019)
[C_3SO_3HMIM]HSO_4	Cellulose	160	30	LA; 36,3%	(Khan et al., 2019)
[C_4SO_3]HMIM]HSO_4	Cellulose	170	300	LA; 41,4%	(Khan et al., 2019)
[SMIM][$FeCl_4$]/H_2O	Glucose	150	240	LA; 67,8%	(Aainaa et al., 2015)
[BMIM][$FeCl_4$]/H_2O	Glucose	150	240	LA;22,4%	(Aainaa et al., 2015)
[SMIM][Cl]/H_2O	Glucose	150	240	LA; 25,8%	(Aainaa et al., 2015)

In the case of liquid membranes, ILs were used to support the membrane by covering it with IL. This combination provided some benefits, including low capital and operational costs, low liquid membrane qualification, low energy consumption, and, most significantly, ease of operation (Xu et al., 2016). This SLM method is known to have broad applications involving all kinds of extraction of organic compounds, especially biomass.

PROSPECTS AND CHALLENGES

Biomass materials, waste, and by-products have been investigated as a viable alternative resource for more than four decades to reduce the world's largest problem in the previous century. This essential study subject is constantly being improved, particularly in terms of the biodegradability of the biomass, which can then be transformed into new biochemical products with a market value.

According to numerous published research, ILs have emerged as a viable and environmentally friendly solvent and catalyst option for enhancing the conversion process of biomass pretreatment. This pretreatment phase in biomass conversion has become critical for increasing the output of bioethanol, LA, or HMF while also increasing the reaction rate. According to several published research, this pretreatment phase is undertaken before beginning the hydrolysis or dehydration process, particularly in the production of LA and HMF. Each type of biomass has its pretreatment procedure determined by the raw component's fundamental state.

These ILs solvents not only break and dissolve cellulose at high concentrations but also be readily recycled after the process, reducing waste. The ILs are referred as green solvents due to their unique characteristics, especially their tunability in polarity, hydrophobicity, and solvent miscibility behaviour, which may be achieved by appropriately modifying their cations and anions. The 1-alkyl-3-methyl-imidazolium halide-based IL is the most promising for use and development in biomass conversion. In the future, the tunability features of ILs in biomass conversion will be critical for selecting the best solvent for each type of biomass material.

Despite the numerous and potential advantages of these ILs, there remain difficulties in this sector. The first issue that has always been considered in the usage of ILs is the expense of this process. Essentially, part of the IL's price is exorbitant when compared to ordinary solvent in the laboratory. This is mostly due to the expensive cost of each IL component and the rigorous purification method available. Therefore, the cost of biomass conversion when using IL as a solvent is 2 to 10 times higher than when using organic solvents, as summarized in Fig. 8. This pricing issue is predicated on carefully selecting the basic cation and anion ILs.

Furthermore, incorporating a recycling process into the entire stage is required to minimize the cost of ILs on an industrial scale. Aside from selecting appropriate ILs, the cost can be reduced by combining existing methods with ILs. This combination approach can enhance product yield because specific conventional techniques have cheaper costs than ILs. The separation and purification of the product solution is the next challenge. Producing a greater yield concentration in the product stream is the best method to address this problem. This approach can assist minimize both the amount of waste solvents and the amount of energy consumed.

According to this review paper, the green synthesis approach, which employs ILs as a solvent, offers a lot of potential for biomass conversion into sustainable products like ethanol and biochemicals. Nonetheless, because of the huge variety of issues that may be researched in the future, this research area is still in its early stages and has a bright future ahead of it.

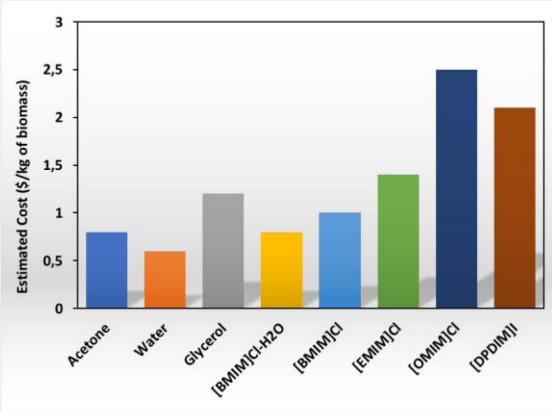

Fig. 8: Cost Comparison of Biomass Conversion Utilizing Organic Solvents and Ionic Liquids. Data Are Collected from (Zunita 2021; Zhang et al., 2014; Brandt et al., 2011).

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