Review Article: Prospect of Deep Eutectic Solvents in Lactic Acid Production Process: A Review

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ABSTRACT

This article reviews the potential application of deep eutectic solvents (DESs) for lactic acid production from lignocellulosic materials where DESs could be used as both preatreatment and extraction solvents as an alternative to the conventional organic solvents and ionic liquids. From literature survey, conventional methods currently explored for lactic acid (LA) production have several drawbacks of low yield, impure LA, low distribution coefficient, high cost of solvents, and non-recyclability of the solvents. Deep eutectic solvents (DESs) is paramount in LA production as could enhance biotechnological development in obtaining higher yield of LA through better recovery as compared with the conventional extraction methods. The prospects of using DESs for LA production is huge in that, their unfavorable properties can be overcome by tailoring them through changing the nature of the molar ratio of hydrogen bond acceptor (HBA) to hydrogen bond donors (HBD), by adding appropriate amount of water if the DESs is highly viscous, by changing temperature or pressure and formation of ternary deep eutectic solvent through combinations of more components. DESs differs from the conventional organic solvent and ionic liquids as it offers several advantages of recyclability, biodegradability, less volatile, non-toxic, non-flammability, high tuneability, high dissolution capability, ease, short time of preparation, and low costs as both pre-treatment and extraction solvents, but its feasibility for LA production has not been tested yet.



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1. Introduction

he increasing demand of lactic acid (LA) is due to its wide applications in production polylactic of acid, cosmetics, pharmaceutical, food and beverages as well as the increasing adoption for eco-friendly packaging materials. Numerous challenges and limitations have been identified during production and purification of lactic acid from fermentation broth using the conventional methods. Thus, to increase yield and purity of lactic acid, green solvents as substitutes for volatile organic solvents (VOCs) and ionic liquids (ILs) should be sought for and the need for shift towards green solvent should be the central focus of researchers supplemented with the novel efficient pretreatment methods as well as solvents with minimal or without generation of hazardous byproducts and innovative lactic acid bacteria (LAB) strains have to be developed to assure efficient lactic acid production [1].

Lactic acid is a water soluble organic compound produced via breakdown of carbohydrates [2]. It has a general molecular formula of CH₃CH (OH) COOH, white in solid state, colorless in liquid state and miscible with water [3]. Lactic acid is chemically known 2as hydroxypropanoic acid, additionally called milk acid and the majorly occurring carboxylic acid in nature that found applications in many industries [1]. Lactic acids is one of the most essential platform chemical for production of products in food, pharmaceutical, diverse textile, chemical, and cosmetics industries, and also used for production of poly lactic acids which is also a platform material in polymer industry [4]. According to Battula et al. [5], lactic acid is a basic chemical used as feedstocks different products for producing via fermentation process. It was reported initially that lactic acid was observed to be found in milky by Scheele when he initially discovered it in 1780. By 1789, it was named as Acide lactique by Lavoisier, while Charles. E Avery was the first to commercially produce lactic acid in 1981 in Littleton, Massachusetts, the USA [1]. It is an organic acid containing a dual functional group: hydroxyl and a carboxylic acid, as displayed in **Figure 1**.

Due to its versatile applications in biotechnology, the demand of lactic acid is on the increase globally. However, the increasing adoption for eco-friendly packaging and the expanding scope of lactic acid utilization in enduser industries are two reasons that will provide a large market opportunity. However, raw material processing price fluctuation is a key stumbling block to market expansion [6].

2. Lactic Acid Market

According to USA based research website, researchandmarket.com. from 2015 to 2022. the market is expected to increase at a compound annual growth rate (CAGR) of 16.9%, from USD 1,275.00 million in 2014 to USD 4,129.19 million in 2022. The worldwide lactic acid market was 750.00 kilotons in 2014 and is expected to reach 1,844.56 kilo tons by 2022, increasing at a CAGR of 12.9 percent from 2015 to 2022. They also reported that food and beverage applications had the biggest piece of the market pie in 2014, preceded by industrial applications. In 2014, the food and beverage category accounted for more than 40 percent of the total pie. Industrial applications, on the other hand, are expected to grow the fastest. From 2015 to 2022, it was expected to expand



Figure 1. Structure of Lactic acid

at a CAGR of 18.3%. By 2028, the worldwide lactic acid market is estimated to be worth USD 5.02 billion, while from 2021 to 2028, it is anticipated to grow at an annual rate of 8.0 percent [GVR, 2020]. The rising demand for lactic acid in different end-use sectors, such as industrial. food and beverages, and pharmaceuticals, may be linked to the market's expansion, particularly in emerging nations such as India, China, and Indonesia [GVR, 2020]. Furthermore, demand for this product as a feedstock in the manufacturing of polylactic acid (PLA) is expected to boost the global market. PLA became the most popularly applied material of industrial importance in terms of volume and income in 2020, mainly to its increasing use in the production of biodegradable and biocompatible goods [1].

GVR, [7] reported that polylactic acid is becoming a major applications accounting for about 30% of LA as of 2018 as a results of its wide applications in packaging, agriculture, 3D printing, textiles and filaments with packaging expected to continue to be the largest application because of its thermal and mechanical properties display by PLA, and thus makes it suitable material for packaging. The quest for renewable material has become the focus of researchers in an effort to shift a fossilbased society towards a sustainable and carbon-neutral society [8]. Hence, lactic acid (LA), a biodegradable raw materials derived from renewable resources, represent a promising substitute to replace the standard petroleum-based polymeric materials as it is used for production of polyester, a major material for production of polymeric materials [9]. Food industry is the second largest user of LA with 26% followed by pharmaceutical industry of 20% while cosmetics and chemical industries accounts for about 14 % and 10% of the total LA produced annually. Table 1 presents the summary of application of lactic acids in various industries.

Table 1. Summary of application of lactic acids in various i	industries
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Field	Percentage of used lactic acid	Applications
		Food containers
Doly lastic acid (DLA)	30	Rigid containers
Poly lactic acid (PLA)	50	Protective clothing
		Trash bags
		Surgical sutures
		Dialysis solution
Pharmaceutical	20	Parenteral/Intravenous solution
industry	20	Prostheses
		Controlled drug delivery systems
		Mineral preparations
		Humectants
	14	
		Skin-lightening agents
Cosmetic industry		Anti-acne agents Moisturizers
		pH regulators
		Anti-tartar agents
		Anti-tartar agents
		Mineral fortification
		Preservatives
Food industry	26	Bacterial inhibition
		Acidulants
		pH regulators
		Cleaning agents
		Neutralizers
Chemical industry	10	pH regulators
Chemical moustly	10	Green solvents
		Descaling agents
		Chiral intermediates

Lactic acid has a huge industrial applications. and as a result, demand is expected to grow in the future. From history, lactic acid is manufactured from materials such as diary waste (whey, skim milk, and paneer whey), starch, glucose, molasses, and lactose [10]. These substrates provide the benefit of generating pure LA without the requirement for pretreatment, as well as lower recovery costs [11]. However, the uses of traditional feedstocks contend emulously with the supply of foods and feeds hence making production cost very high. Therefore, producing lactic acid via cheap carbon sources and huge agricultural waste has now become alternative sources for lactic acid production [12]. Feedstocks like refined sugar such as glucose or sucrose sources used in the production of lactic acid required high amount of expensive nitrogen (yeast) so as to produce LA which is not economically suitable [12]. Thus, the need to consider lignocellulosic materials as а substitute for refined sugar. According to Coelho et al. [13], raw materials account for about 68% of total cost of lactic acid production. As a result, research is being directed towards using inexpensive, renewable, and sustainable lignocellulose biomass as a competitive and ecologically acceptable alternative [1]. Lignocellulosics materials are one of the major abundant renewable resources currently. It consists of cellulose, hemicellulose, and lignin. Cellulose is homopolymer of glucose in the form of crystal and it is resistant to depolymerisation, while hemicellulose is amorphous and heteropolymer containing C_5 and C₆ sugar with Xylan being the main component [10]. Depolymerization of glucose polymers to produce fermentable sugars is necessary for microbial fermentation. Hence, pretreatment of lignocellulosic materials is [14]. Lignocellulosics paramount has advantages of not competing with food crops such as corn, rice, cassava, and sorghum. It is the widely spread, abundant, inexpensive, and renewable feedstock for large scale production and contain high glucose content compared to starchy crop [11]. Thus, some agricultural wastes such as sugarcane bagasse, corn cob, banana peel, rice husk, microalgae, etc. need to be examined as feedstocks for lactic acid

production. A huge variety of microorganisms including bacteria, fungi, microalgae, yeast, or cyanobacteria may be used to manufacture LA by means of fermentation [15]. However, research on the usage of lactic acid bacteria (LAB) accounts for approximately 90% of the literature on the LA production. This is because of their potential to produce LA at very high yields and productivity [16]. Lactic acid microorganism (LAB) is various series of microorganisms that make contributions to a huge variety of fermentation activities [1]. They stated that because of the well-documented health-promoting characteristics of some LAB, probiotic cultures including chosen strains in conjunction with bifidobacteria have been developed for use in the food sector. Grampositive, non-sporing, non-respiring cocci or rods that generate lactic acid as the primary product during the carbohydrates end fermentation are the bacteria that make up this category. LA is produced from petroleumderived compounds or from natural substrates fermented by microbes [17]. The chemical method uses acetaldehyde and hydrogen cyanide in the presence of a base to generate lactonitrile, which is subsequently hydrolyzed to yield *D/L*-LA combinations. Because the pure isomers have specialized industrial uses, the racemic mixture has less industrial value than the pure isomers [1]. Because it can be digested by the human body, the L (+)-LA is highly after the medical. sought in food. pharmaceutical, and cosmetic sectors. Increased levels of *D* (–)-LA, on the other hand, may be detrimental to the human body [18]. The conventional purification of lactic acids by precipitation as calcium lactate produces huge quantity of gypsum (CaSO₄), which results in low yield and productivity of LA, and also generates environmental problem since the large amount of (CaSO₄) is greater than LA produces, and thus hindered the economic and commercial production of lactic acid through this process [19]. However, from literature, the better option and alternatives for purification of lactic acid is solvent extraction, but solvent extraction efficiency is limited by high toxicity of conventional organic extraction agent, and thus developing an efficient separation and purification techniques that lower the cost of

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production of LA from the fermentation broth is a major challenge hindering lactic acid productivity and yield [20]. Conventional organic solvents usually have the problem of high toxicity, volatility, cost, and nonbiodegradability [2]. ILs have gained a lot of attention because of their non-volatility and negligible vapour pressures; however, they have limitations of high cost, complex synthetic, purification procedures. low moisture tolerance, toxicity, and biodegradability [21]. Till-date, various methods have been tested for the LA production from the fermentation broth to reduce production costs, amount of effluents, and thus decreasing the negative impact towards the environment [22]. Precipitation, adsorption, solvent extraction, reactive distillation, and membrane separation process are some technologies used as an alternative for the conventional process [3]. Despite these approaches been utilized, there is need to improved lactic vield through acid environmentally friendly and low-cost means through the DESs uses. Although, from literatures, the DES uses as extractant and pretreatment of lignocellulosics feedstock for lactic acid production have not been widely and efficiently investigated. The aim and objectives of the paper to review the various methods that have been used for production of lactic acid and highlight the promising biotechnological solutions that deep eutectic solvent offers in solving the persisting problems of inefficient LA

production and how DES can significantly reduce production costs of LA from local materials. Also, this review is aimed at inspiring researchers towards the uses of novel solvent in lactic acid production and to persuade government and non-governmental organizations to provide financial assistance. **3. Deep Eutectic Solvents (DESs)**

Interest in developing and advancing more efficient solvents has been the focus of researcher lately due to need for greener solvents of green chemistry. DES is a liquid that is usually made up of two or more compounds that can self-associate, often by hydrogen bond interactions, to form a eutectic mixture with a melting point lower than the melting point of each individual component [23]. Deep Eutectic Solvents (DESs) constitute an organic salt with negligible vapor pressure and is nonflammable which are suggested substitutes for volatile conventional organic solvents [24]. DESs has several applications as it can be used for CO_2 capturing, metal processing, extraction/separation, solvent electrocatalysis, development/reaction medium, electropolishing, electrochemistry, hydrometallurgy, and as catalyst, or catalyst carrier, etc. [21]. Figure 2 depicts the total publication of DESs from 2004 to 2020 indicating the rapid acceptability and versatility novel of this green and solvent.

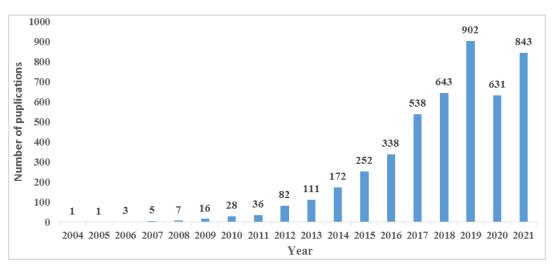


Figure 2. Total publications for DESs by 2021 [25]

The DES uses for biotransformation are gaining a lot of interest owing to its action on enzymes like cellulose, lipase, and protease, etc. Thus, there is a need to evaluate biological interactions of DESs and their utilization in biotransformation. DES is similar to ionic liquids; however, ionic liquids (ILs) were introduced as substitutes for the conventional organic solvents [24]. This is as a result of their low vapor pressure [26]. Thus, a new and recent group of solvents similar to ionic liquids were introduced by [23] in 2004 and referred to it as "deep eutectic solvents" (DESs). DES is a combination of hydrogen bond donor and hydrogen bond acceptor at a temperature lower than the temperature of individual components. Furthermore, deep eutectic solvent has some such characteristics essential as nonflammability, low toxicity, high tuneability, low vapor pressure, high biodegradability, and good biocompatibility [24-27]. These important features of DES increase their potential utilization in various biochemical applications when compared to ionic liquids or conventional organic solvents [28]. Traditionally, although biotransformations have been performed in conventionally organic solvents such as methanol, hexane, and acetone, they normally cause enzymes denaturation [24]. Where DES dissolves the substrates without enzyme activation [24]. The aim of this review is to highlight the DES importance as a substitute in the production of lactic acid from agricultural feedstock. Lately, from literature DES have displayed good results in different biotransformation reactions. For example, DES have been successfully established as solvent for various chemical reactions such as metal electro-deposition [29] and enzyme-catalyzed

reactions [30-32] and in liquid separation and nanoparticle functionalization [33]. DESs have been further applied as green solvent for extraction in biological materials including DNA and RNA [34-35]. From literature to the best our knowledge, DES has not been used to produce lactic acid. DESs are classified into the following four different types based on the components mixed. Table 2 provides various types of DESs and their typical HBAs and HBDs DESs samples can be synthesize in different molar ratios of hydrogen bond acceptor (HBA) i.e. Choline Chloride (ChCl) and hydrogen bond donor (HBD) such as urea, glucose, sorbitol, oxalic acid, glycerol, ethylene glycol, etc. in an incubator shaker at an appropriate molar ratio. 3.1. Preparation of deep eutectic solvents

There are two methods of preparing deep eutectic solvents (DESs); a vacuum evaporation and a heating technique. Vacuum Evaporation technique: Various components at appropriate molar ratios are dissolved in water and evaporated at 50 °C with a rotary evaporator. The liquid solution is then covered with silica gel into a desiccator until they reach a regular weight. Heating technique: this technique is used to prepare DESs with a known quantity of water. The two-component mixture with calculated quantities of water is positioned in a beaker with a stirring bar and cap and heated in a waterbath at a temperature range of 50 °C to 80 °C with continuous agitation until a clean homogeneous liquid is formed, normally approximately 30-90 min) [36].

Figure 3 demonstrates a typical combination of two component form a deep eutectic solvent.

Types of DESs	Hydrogen bond acceptors	Hydrogen bond donor	Example
Type 1	Quaternary salt	Metal chloride	Choline chloride (ChCl) + AlCl ₃
Type 2	Quaternary salt	Hydrated metal chloride	$ChCl + MgCl_2 \bullet 6H_20$
Type 3	Quaternary salt	Hydrogen bond donor	Choline Chloride + Urea
Type 4	Metal chloride	HBDs e.g. Urea	Urea etc

Table 2. Various types of deep eutectic solvents and their typical combinations

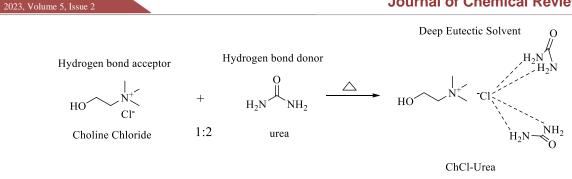


Figure 3. A schematic illustration of two component form a deep eutectic solvent (Choline chloride-urea) [29]

Physicochemical and thermal properties of DESs will can enhanced pretreatment and extraction includes; pH, solvatochromic parameters, refractive index (RI), density ,surface tension, freezing temperature (Tf), viscosity, decomposition temperature (Td), octanol-water partition coefficient (Kow), flammability, and miscibility [21]. These properties depend on the composition and types of DESs used. Key advantages of DESs over the conventional volatile organic solvent used in lactic acid production includes recvclability [21], biodegradability, less volatile, and non-toxic [37].

The preparation of DESs is simple; no solvent or product purification step is required because no by-products are formed [38]. They are analogues to ionic liquids (ILs) but an enhanced ILs. DES is formed by cation, anion, and complex agents, while ionic liquids are formed by cation and anion only. Deep eutectic solvent has some essential characteristics such as nonflammability, high tunability, low vapor pressure, high biodegradability, low toxicity, and good biocompatibility [24-27]. They have high dissolution capability, i.e. their ability to donate and accept protons and electrons, which facilitates the formation of hydrogen bonds between molecules.

Payam and Ghandi [39] also reported that DESs is attracting more attention as green solvents, owing to their characteristics like ease and short time of preparation, low toxicity, good biodegradability, and low costs. DESs can also be used for extraction of essential chemicals from biomass, and thus can be used to overcome the challenges of separation and purification of sugar based chemicals from lignocellulosics materials since its guarantee only the dissolving of sugar molecules in

biomass rather than further conversion into the undesirable products [36]. DESs have been used for pretreatment of biomass, especially carbohydrates since various conventional solvent like H₂SO₄, trifluoroacetic acid, KOH, and ionic liquids have been utilized and they are toxic, high cost, not environmentally friendly. Also, higher value of hydrogen bonding enhanced easy break of lignin in the cellulose [24]. Utilization of DESs for treatment and conversion of lignocellulosics materials are attracting more attention. Ren et al. [40] produced а DES; allyltriethylammonium chloride: oxalic acid at ratio of 1:1 for pretreatment of cellulose and they were an enhanced solubility of 64.8%. Sirviö et al. [41] utilized Choline chloride: Urea (molar ratio of 1:2) DESs for pretreatment of cellulose into individual nano-filbrils and reported that it is a new way of achieving nanofibrils cellulose without cellulose without chemical mechanical modification of cellulose. They observed that Choline chloride: Urea preremarkably treatment improved nanofibrillation of the pulps compared to when using NaOH as solvent. The uses of DESs for lactic acid production have not been tested. They also stated that DESs can serve as solvent and catalyst for the production of bioactive compounds. In their work, they applied three DESs namely; ChCl: urea CCU, ChCl: oxalic acid CCO, and ChCl: glycerol CCG to examine the isomeric distribution of xylose, fructose, Nacetyl-D- glucosamine and glucose in D_2O . Hence, there is potential, that DESs can be utilized with glucose to produce derivatives such as lactic acid. Wang et al. [42] reported that DESs has a good interaction with enzymes and microorganism hence a good solvent for pre-treatment, extraction, separation, and

purification processes to produce valuable products from plant biomass. The intramolecular hydrogen bonds in them which aid in breaking hydrogen bond in lignocellulosics materials and thus make these materials soluble and high conversion into useful products [36]. **Table 3** lists several studies on different applications of deep eutectic solvents.

Types of DESs	Methods/ approach	Applicatio ns	Key findings	Remarks	Referen ces
not defined	Theoretica l approache s/review	Pre- treatment, extraction and catalysis	Deep Eutectic Solvents has potentials for Pre- treatment, Extraction, and Catalysis of Biomass and Food Waste: A review	The feasibility of DESs for LA production needs to be investigated.	[39]
not defined	Theoretica l review/Ap proaches	Pretreatme nt of biomass	They reported that microwave-assisted deep eutectic solvent pretreatment is extremely fast and produces little to no harmful by-products, but it has not been investigated for lactic acid production yet.	The need to investigate the feasibility of DESs as pretreatment solvents.	[1]
Hydrophobic borneol-based natural DES (decanoic acid, borneol and oleic acid) (1:2, 1:31:4) and borneol with thymol (1:1, 1:2, 1:3 and 1:4)	Experimen tal study approache s	Extraction	They studied Hydrophobic borneol- based natural deep eutectic solvents as a green extraction media for air- assisted liquid-liquid micro-extraction of warfarin in biological samples.	Applications of DES can be tested for extraction of other biological chemicals like LA.	[43]
Natural deep eutectic solvent (NADES) composed of choline chloride and sesamol (1:3)	Experimen tal study approache s	Vortex assisted Liquid- liquid micro extraction	They reported a high extraction efficiency (near 100%) of food toxicant in food samples via liquid microextraction (VALLME).	There is need to investigate the wide application of these novel chemical in synthesis of other platform chemical such as LA.	[44]
DESs (Choline Chloride -Urea)	Experinme ntal Study / Approache	Pretreatme nt of rice straw	They carry out pre- treatment on of rice straw after with a deep eutectic solvent of choline chloride/urea.	Pretreatment of other agricultural residues such as corncob and bagasse can be analyzed.	[45]

Table 3. Several studies on different applications of DESs Matheds (

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not defined	Theoretica l review/Ap proach	Pretreatme nt of biomass	They explained recent trends concerning the uses of DESs as pretreatment and they highlight the advantages of DESs over conventional solvent.	There is need for experimental validation and investigation of DES for pre-treatment of biomass.	[37]
DESs (C5H14ClNO : C2H6O2) 1 : 2) and K2CO3 : C2H6O2 = 1 : 10)	Experimen tal approach	DESs for application of biodiesel production	DES improved the purification of biodiesel compared to using organic solvent such as KOH.	Other applications of DESs for purification of bioactive compound such as LA can be investigated owing to their unique properties.	[46]
not defined	Theoretica l review/Ap proach	biomass pretreatme nt and conversion	They reported an overview of application of DESs for the pretreatment of biomass and conversion of biomass to value-added products.	There is need for experimental investigation to validate the theoretical claim.	[36]
DESs (Toluene + heptane+ (tetrbutylphosphoni um bromide: ethylene glycol), toluene + heptane + (tetrbutylphosphoni um Bromide: sulfolane).	Experimen tal approach	liquid- liquid extraction of aromatic compounds	Demonstrated that DESs have the advantage over conventional extraction solvents for seperating aromatic hydrocarbons due to their ease of synthesis, tunable physical properties, and high selectivities in extraction experiments	Applications of DESs for LA production can be investigated owing to their properties.	[47]
not defined	Theoretica l approach	Intensificat ion of biotransfor mations using deep eutectic solvents	They reported a presentation about the status of biological interactions of DESs and their application in the field of biotransformation.	Efficacy of DESs can be evaluated for biotransformation in verse area of application.	[24]
not defined	Theoretica l approach	wastewater treatment and resource recovery	It revealed that the performance of greener organic solvents (mixed conventional-green and sole green organic solvents) for treatment of waste water.	DESs can be investigated for extraction solvent due to their tuneability.	[48]
Tetrabutylammoniu m Bromide (TBABr)- DESs Based (tetrabutylammoniu m bromide (TBABr) : ethylene glycol, 1,3-propanediol, 1,5- pentanediol and glycerol	Theoretica l approach	Determinat ion of Physical Properties of TBABr based DESs	They measure the physical properties of the synthesized DESs.	The feasibility of DESs for LA production needs to be investigated owing to their unique physicochemical properties.	[49]

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Hydrophobic (HDESs)	Theoretica l approach	Microextra ction	Outlined a comprehensive summary of available literature data on the most important physicochemical properties of HDES playing a key role in aqueous sample preparation methods.	The need for experimental investigation of the hydrophobic DESs to test their application in LA production.	[50]
DESs Choline chloride Lactic acid 1:1.Choline chloride Malonic acid 1:1 Choline chloride Citric acid 1:1, 2:1,	Experimen tal approach	solubilizati on of wide range of biomolecul es such as non- water soluble bioactive natural products, gluten, starch, and DNA	They concluded that the novel NADES may be expected as potential green solvents at room temperature in diverse fields of chemistry.	Applications of NADES for extraction of LA can be investigated owing to its ability to solubilized bioactive compounds.	[51]
NADES (Lactic: Bet (2:1) (lactic acid/betaine), Lactic :Hist (9:1) (lactic acid/histidine), Ma:Bet:H2O (1:2:3) (malic acid/betaine/water)	Experimen tal approach	Characteriz ation of acidic based DESs	They carried out Synthesis and physical and thermodynamic properties of lactic acid and malic acid-based natural deep eutectic solvents.	Application of acidic based DESs for LA production can be evaluated to due to their favorable physicochemical characteristics established.	[52]
(Cholinium Chloride and Carboxylic Acids)	Experimen tal approach	Synthesis and characteriz ation of DESs	They provides physicochemical characteristic of the synthesized DESs.	Applications of DESs for LA production as a result of their favorable characteristics.	[53]
Choline chloride: monocarboxylic acid, Dicarboxylic acid/ choline chloride and polyalcohol/.	Experimen tal approach	Pretreatme nt of corn cob	They obtained pretreatment optimum condition of 90 °C and 24 hours	Application of DESs for bioconversion of waste to useful product is necessary since it is a suitable solvent for pretreatment.	[54]
not defined	Theoretica l approach (review)	Biomass fractionatio n and conversion to bio- based products	They examines several studies on raw materials lignocellulosic biomass fractionation using DES and their conversion into bio-products.	The review calls for consideration of application of DESs for LA production.	[55]

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DESs (Choline chloride-Urea, Glycerol)	Experimen tal approach	Structures and dynamics of DESs	They investigate the structure and dynamics of deep eutectic solvent using infrared spectroscopy.	The potency of DESs for LA production can be analyzed owing to their properties.	[56]
DESs	Theoretica l approach	Role of water in DESs	They examine the role of water in deep eutectic solvent-base extraction.	The knowledge of role of water in DESs extraction will aid extraction of LA using DESs.	[57]
not defined	Theoretica l approach (review).	Extraction of biochemica l compounds such as proteins, nucleic acids	They carry out an overview on interactions of DESs with water and their applications for biochemical compounds.	Utilization of DESs for LA has not been carry out and can be done because of their excellent interaction properties.	[58]
not defined	Theoretica l review (approach)	Synthesis of bio compounds , pharmaceu tical industries.	They concluded DESs has potentials application in different field of study.	Experimental investigation is necessary to evaluate the efficacy of DESs for LA production.	[59]
(choline chloride/ maleic acid, choline chloride/resorcinol, choline chloride/phenol and choline chloride/alpha- naphthol)	Experimen tal study	Cellulose dissolution	Cellulose was found to be dissolved in these DESs by the use of ultrasound irradiation.	Since cellulose was found to dissolve in DESs, its application for LA production can be investigated.	[60]
DESs (choline chloride and imidazole)	Experimen tal study	Dissolution of lignocellulo sics biomass	They obtained higher solubility of 4.57 wt% in choline chloride – imidazole.	Since DESs can dissolve cellulose, it can serve as a potential solvent as pretreatment and extraction solvents.	[40]
not defined	Experimen tal study	Pretreatme nt of biomass	DESs caused delignification and reduced crystallinity of cellulose when used for pretreating biomass.	Delignification of biomass is necessary to analyze the feasibility of their uses in LA production.	[61]
(Choline chloride and phenol Choline chloride-p-coumaric acid)	Experimen tal study	Delignificat ion of biomass	They obtained maximum delignification of 60.8%.	Delignication pave way for hydrolysis, hence, feasibility study of DESs for LA production via fermentation can be investigated.	[62]

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DESs	Experimen tal study	pH behavior of DESs	They concluded that pH of DESs decreases as temperature rises.	Application of DESs can be tested for its use as extraction solvent for LA.	[63]
DESs (ChCl-formic acid and ChCl-lactic acid-acetic acid)	Experimen tal study	Pretreatme nt and biochemica l conversion	DESs showed the excellent performance in enhancing switchgrass digestibility.	Use of DESs for LA production can be investigated owing to its for biochemical conversion.	[64]
DESs	Experimen tal study	Determinat ion of physical properties of DESs	Properties such as decomposition temperature, surface tension, density, and viscosity were measured.	Physicochemical data of DESs are necessary to analyze the feasibility of their uses in LA production.	[65]
not defined	Theoretica l approach		They give an overview of acidic based DESS and their application.	The feasibility of DESs for LA production can be evaluated.	[66]
(triethylbenzyl ammonium chloride/lactic acid 1:5)	Experimen tal study	Lignin extraction	They obtained 79 % of lignin removal at 373 K and 10 hours for wheat straw.	Uses of DES can be investigated for other biomass such as corn cob, bagasse and their feasibility for LA production.	[67]
(lactic acid and malic acid-based (2:1)	Experimen tal study	Physicoche mical and thermodyn amic characteriz ation of DESs	They carried out a comprehensive Physicochemical and thermodynamic characterization of DESs.	Physicochemical and thermodynamic data of DESs are necessary to analyze the feasibility of their uses as extractant in LA production.	[68]
(malic acid and proline)	Experimen tal study	Dissolution of lignocellulo sics biomass	The maximum solubility of cellulose was found to be 0.78 wt%.	DESs has potential to be used as a suitable solvent for LA production owing to their solubility in biomass.	[69]
DESs (lactic acid- ChCl and lactic acidbetaine)	Experimen tal study	Delignificat ion of rice straw	About 60% of lignin was found to be removed from the rice straw.	Application of DESs for LA can be investigated owing to the positives characteristics of DESs.	[70]

Among several studies carried out with regards to the use of deep eutectic solvents (with details presented in **Table 3**). Some of the application of DESs considered entails pretreatment of delignification biomass [21-54], of lignocellulosics materials extraction [43-59], synthesis and physicochemical characterization of DESs 46-68, biodiesel production [46], synthesis of bio compounds such as protein [64], and cellulose dissolution [40-69]. From literature and to the best our knowledge, deep eutectic solvent has not been used for production of lactic acid. Hence, there is need to carry out feasibility studies and an investigation into the production of platform bio compounds like lactic acid owing the potentials of its physicochemical characteristics such as biodegradability, less toxicity, non-volatile, cheap, recyclable, and highly tuneable unlike the conventional solvents that have been utilized in the production of lactic acid. Likewise, DESs ability for cellulose dissolution boost further prospects of its used in production of bio compound such as lactic acid. Further survey of literature has unveiled several works that did not pay attention to the optimization and kinetics studies of DESs application for delignification, extraction, etc. which are necessary for establishment, commercialization, and scale up of pilot plant of such production process like lactic acid from lignocellulosics materials. No literature has considered the feasibility of pilot study of DESs for extraction and pretreatment. Furthermore, there is no literature currently establishing the techno-economic analysis of the uses of DESs as a substitute for conventional and ionic liquid used for several applications. Despite the existing application of DESs for biomass treatment and conversion into valuable products, there are many contingencies for designing more efficient DESs as a result of complexity of biomass. Moreover, the major producing most bioactive challenges in compounds are in the purification stages. Hence, the need to develop a solvent that can give high purity and better extraction efficiency of these valuable compound such as lactic acid.

4. Lactic Acid Bacteria (LAB)

Microorganisms that are capable of producing LA are: Bacteria fungi and yeast. Lactic acid bacteria refer to collection of gram-positive, non-spore, and rod-shape bacteria belonging to the genera set of *Atopobium*, *Lactobacillus* (*LB*), Aerococcus, etc. [71]. One of the key reasons for the use of bacteria for lactic acid production in industry is because they do not have negative health effects compared to fungi and yeast [72]. Examples of lactic acid bacteria (LAB) are Bacillus strain. Escherichia coli. L-casei. Ldelbruki, etc. [72]. LAB can produce LA anaerobically via glycolysis with high yield and productivity. The main disadvantages of using fungi for LA production is that more byproducts (tamaric acid and ethanol are produced than the desired LA [11]. Based on the end product, LAB can be group into the followings:

4.1. Homofermentative LAB

This produces lactic acid as the major output from sugars e.g., Bacillus coagulan, *L*-casei, *L*-delbruki, and L-bulgaricus.

4.2. Heterofermentative LAB

This produces less yield of LA due to production of by-product such as ethanol, acetic acid, and CO_2 e.g. *L-acidophilus*. Advantages of *Bacillus coagulans* over other LABs includes low nutrients demand, it can withstand low to moderate temperature fermentations, give high optical purity of LA, ability to utilize both hexose and pentose, undergoes homo-lactic fermentation and exhibit less glucose repression compared with other LAB [10]. **5. Lactic Acid Production**

There are basically two methods of producing LA. These are fermentation and chemical methods as depicted in **Figure 4**.

5.1. Chemical method of lactic acid production

Here, acetaldehyde is the starting material for the chemical route. Figure 4 demonstrates the LA synthesis via chemical method. Providing a racemic mixture of LA, where hydrogen cyanide is added along with a base to produce lactonitrile at an elevated atmospheric pressures, accompanied by distillation to recover the lactonitrile crude, and hydrolvsis with concentrated sulphuric acid, to give lactic acid and ammonium salt [73]. Furthermore, to achieve a higher purity, the lactic acid reacts with methanol to produce methyl lactate, passing through a distillation step to be further hydrolyzed by water, obtaining lactic acid and methanol [8].

5.2. Fermentation method of lactic acid production

This method of production of LA involves the uses of bacteria via fermentation process using

carbohydrate sources containing C_5 and C_6 sugars [74]. It is the most frequently used method or industrial production of LA because of high yield and purity. Lactic acid produced via fermentation has several merits over the chemical synthesis route as the former has low energy consumption due to low temperatures employed, it is more cost effective and availability of a wide range of low-cost substrates [13-76]. According to Ajala *et al.* [1] close to about 90% of LA production globally is methods. via fermentation Lactic acid fermentation hinges on factors like the lactic acid bacteria used, feedstock, and nutrients present in the media [5]. There are mainly three methods of fermentation process which includes continuous, batch and fed-batch fermentations. Figure 4 show the various step in production of lactic acid via fermentation and chemical methods.

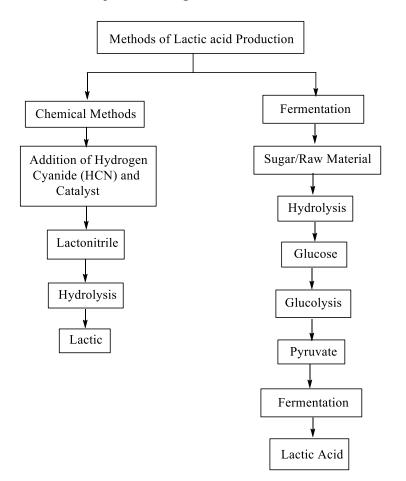


Figure 4. Process steps for production of lactic acid via different methods

The following steps show the mechanism of LA production via the conventional method:

Fermentation: Under anaerobic condition, glucose is broken down into LA.

 $C_6H_{12}O_6 \longrightarrow 2C_3H_6O_3$ (1) Sugar lactic acid *Neutralization*: LA is neutralized by Calcium hydroxide during fermentation

 $2C_{3}H_{6}O_{3}+Ca(OH)_{2}$ \longrightarrow $Ca(C_{3}H_{5}O_{3})+2H_{2}O...(2)$

Lactic acid Calcium hydroxide Calcium lactate water

Acidification: Sulphuric acid is added to precipitate gypsum and filtered

 $Ca(C_3H_5O_3) + H_2SO_4 \longrightarrow 2C_3H_6O_3 + CaSO_4....(3)$

Calcium lactate/Sulphuric acid/lactic acid/ (Calcium sulphate) [5]

5.3. Downstream process of lactic acid (Purification)

Presently, calcium lactate, is the most widely used purification method for lactic acid production; a process involving calcium hydroxide precipitation and it has been applied by the world largest producer of lactic acid; Nature Works and Purac in lactic acid production from starch [77]. However, this method is limited by high consumption of sulphuric acid, generation of gypsum, and low productivity of LA. It has been a challenge to efficient and cost-effective design an downstream process for lactic acid purification. Not only due to the strong affinity of LA towards water, its low volatility, and its probable decomposition when it is exposed to the elevated temperatures, but also due to the presence of various organics acids in the fermentation broth that present similar properties to LA [78]. Making conventional separation approaches such as distillation or solvent extraction with standard organic solvents unprofitable [8]. Table 4 lists various of recovery lactic acid from methods fermentation broth and the need to use new techniques of deep eutectic solvent as an alternative to conventional methods.

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Membrane filtration is another conventional method of lactic acid production that involves; electrodialysis and nanofiltration present promising results, including low effluent generation, low chemical consumption, and low energy conditions [9]. It can be implemented in situ to remove the lactic acid via fermentation broth continuously, maintaining the operational pH. A double electrodialysis process has been further developed successfully to produce concentrated lactic acid using an initial electrodialysis unit to remove the multivalent ions succeeded by a water-splitting unit with bipolar membranes achieving a high recovery vield. However, Komesu et al. [3] highlighted polarization and fouling problems which limits the application of electrodialysis on a large scale. They also reported that additional process steps should be implemented to achieve lactic acid with high purity for polymerization applications. These additional process steps could make the whole process of using electrodialysis not economically viable hence the need to look for alternative techniques that will give high purity of LA using suitable solvent such as DES. Solvent extraction efficiency is limited by high cost and toxicity of conventional organic extraction solvents such as acid and base. Hence, the need to use green solvent (DESs). Joglekar et al. [79] stated that in terms of obtaining high purity of lactic acid, reactive distillation becomes an attractive alternative, where the lactic acid reacts with alcohol, followed by a distillation of the ester and hydrolysis to obtain the free lactic acid and alcohol. They noted that esterification is the best option for downstream processes that allows the separation of lactic acid from other organic acids, due to the differences in boiling points of their ester compounds [78]. Generally, distillation this reactive presents thermodynamics limitations, therefore, excess amount of alcohol and rapid removal of water are common practices to obtain high yields (between 60% to 100% - depending on the implemented removal method). water However, the presence of impurities in the feed

Table 4. Various methods of recovery lactic acid					
Methods	Advantages	Disadvantages	References		
Precipitation	Easy process, low energy requirement, and simple operation.	Consume high sulphuric acid, generate calcium sulphate with some organic impurities making it harder to dispose of, low product purity and high cost of reagents.	[3-8]		
Membrane separation	Low effluent generation, low chemical consumption, possibility of integrating with conventional fermenters, low energy conditions, easy to operate, and high selectivity.	Polarization and fouling problems, it requires additional process steps hence not economically viable, and high cost of membrane.	[2-9]		
Distillation	No other purification step is required, gives good product purity and no uses of solvents.	High energy requirement, Presence of impurities in the feed stream such as residual sugars and proteins affect the performance of the catalyst, complex process, difficult to scale up, required high vacuum condition, applied specifically to reversible reaction in liquid phase, corrosion, and separation problem when homogenous catalyst are used.	[78- 79]		
Extraction	Gypsum are not generated, require low energy consumption.	Conventional extraction solvent shows unfavorable distribution coefficients, they are toxic, cost non-recyclability, and biodegradability of the solvents.	[3- 11]		
Adsorption	Good product purity.	Short existence time of adsorbent, extra filtration steps, negative potential regeneration of ion exchange resin, selectively of adsorption resin, and challenges in regeneration of activated carbon.	[3-39]		
Ion exchange	Ease of controlling pH and no uses of solvents.	generation of high quantity of the secondary waste, required additional unit operations, and use of large quantity of chemical at some stage in its regeneration step which will all increase its operational cost and reduces purity.	[3-9]		
Ultrafiltration & Electrodialysis	Low effluent generation, low chemical consumption, high LA recovery yield, and low product purity.	Polarization, fouling problems, requires additional process steps, high production cost, and difficult to scale up.	[3-80]		
Crystallization	High selectivity.	Difficult to scale up and required further process step; hence, not economical.	[8- 81]		

Table 4. Various	methods of recovery lactic acid
dvantages	Disadvantages

stream such as residual sugars and proteins affect the performance of the catalyst, cation exchange resins, complicating steady state operation [78].

According to Urrea [8], some downstream processes that can be used to separate and purify lactic acid via the fermentation broth in industrial processes has been elucidated and that some improvements to the conventional method have been found over the years, but still, there is need to further investigate others

means of production of lactic acid and the need to develop a more efficient and economically attractive process potentialize the to production of lactic acid. Based on the report of Joglekar et al. [79], several techniques for separation and purification have been suggested in literature. However, the common method involves lactic acid precipitation using calcium hydroxide, while the recovery process is carried out using excess sulphuric acid which generate huge amount of Calcium sulphate as

waste [82]. As a result of chemical use of (H_2SO_4) and $CaSO_4$, the LA purity decreases and making the whole process not environmentally friendly. However, researcher are currently focusing on alternative techniques for recovery and purification of LA from fermentation broth [2].

5.4. Feedstock for lactic acid productionlignocellulosic materials

According to Ameh *et al.* [82] any organic materials available in a renewable form such as food residues, forestry feedstocks, aquatic plants, marine algae, agricultural residues as well as energy crop can be term as lignocellulosics biomass. López-Gómez *et al.* [12] reported that fossil raw materials are being depleted, and this is directing society towards using renewable natural resources to fulfill the growing demand for goods and energy. Moreover, renewable resources are more evenly distributed on earth than fossil resources. Thus, the uses of renewable resources could enhance the use of local resources. Pretreatment of lignocellulosics feedstock is necessary in order to reduce recalcitrance and to enhance the yield of fermentable sugar via enzymatic hydrolysis [83]. According to Krishnan et al. [84], pretreatment of lignocellulosic materials reduces carbohydrate degradation and toxic products after fermentation of microorganisms. Various pre-treatment methods have been used by researchers to treat different lignocellulosic materials [85-86]. Such methods includes physical pretreatment like milling (size reduction) [87] and irradiation [88]; physical and chemical treatments, using water or steam explosion [89], ammonia pre-treatment [87], organic and ionic solvents [90], supercritical fluids, acids / bases, and sulfite pre-treatment [87], nitrobenzene and copper [91], and biological method of pretreatments using bacteria and fungi [92]. Table 5 lists several studies on lactic acid production.

Table 5. Several studies on lactic acid produce	ction
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Substrate	Study Approaches /Methods	Recovery methods/ Type of Solvent used	Fermentation conditions	Key findings/LA yield (%)	Remarks	Refer ences
Corn cob	Experimenta l study via fermentation process	Extraction /Oxalic acid	at 48 hours, 50 °C, and pH of 6.0	They carried out study on delignification of corn cob for the synthesis of lactic acid with 82 % yield.	Purification, kinetics, and optimization of fermentation process were not carried out. Organic solvent was used.	[93]
not defined	Theoretical frame work /study	not defined	not defined	They carried out A review study of LA production to Purification.	Reported that the cost of LA production is limited by downstream processing.	[3]
Yam peel hydrolysat e	Experimenta l study via fermentation	Precipitation /Sulphuric acid H ₂ SO ₄	200 rpm, 35 °C, and 96 hours	80.03%	Conventional solvent was used. No optimization was carried.	[1]
Cassava (Fufu)	Experimenta l study via fermentation	Precipitation	30 °C,pH of 5.5 3000 rpm and 24 hours	At optimum condition, they produced highest yield of LA of 29.5 %.	Kinetics study is necessary for pilot scale study.	[94]
Groundnut shell and Sugarcane molasses	Experimenta l study via fermentation	Micro extraction/ Methanol	42 ºC,pH of 5.5	They obtained LA yield of about 30 g/l from groundnut shells and 23.5 g/lit from sugarcane molasses, respectively.	Organic solvent was used which resulted in low yield of LA from the feedstocks hence the need to improve the yield of LA.	[95]

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Sweet Sorghum Juice	Experimenta l study via fermentation	Ultra- filtration and electrodialys is. chromatogra phy and vacuum evaporation	45 °C, pH of 5.5 and 36 hours.	78.75 g/L, 0.78 g/g. (78.6%).	Filtration has disadvantages of high cost of membrane, difficulty in scale up, fouling, and polarization problems. Optimization and kinetic study of LA have not been carry out.	[2]
not defined	Theoretical (review) frame work/study	not defined	not defined	They conclude that the presence of lignin in lignocellulosics material limit LA conversion and leads to poor digestibility by microorganism.	DESs have potential and can be suitable for pre-treatment of lignocellulosics owing to their properties.	[5]
Cassava bagasse	Experimenta 1 study via fermentation	Precipitation /Sulphuric acid H ₂ SO ₄	pH of 6.5, 42 °C and	They obtained low LA yield of 8.30 % (0.88 g/g).	Pretreatment, optimization, and kinetics studies were all not done which may results to drastic low yield of LA obtained.	[96]
not defined	Theoretical (review) frame work/study	not defined	not defined	They conclude that there is challenges of carbohydrate hydrolysis to release sugar and presence of degradation compound during pretreatment.	Cellulose and hemicellulose are not directly available for bioconversion to LA due to their intimate association with lignin. A novel DES that will be used for pretreatment of substrate for LA to test its efficacy on LA yield.	[77]
Corn cob hydrolysat e	Experimenta l study via fermentation	Precipitation /Hydrochlori c acid (HCl	24 h at 45 ℃ and pH of	They obtained LA yield of 78.81% for mixed glucose and corn cob hydrolysate.	Conventional organic solvent was used for pre-treatment which generate a lot of inhibitory products. They did not carry out purification.	[42]
not defined	Theoretical Approach/R eview	not defined	not defined	They conclude that, challenge facing LA production currently is how to obtain sugar of high concentration in a cost effective way.	Efficacy of DESs as pretreatment solvent for biomass conversion into LA can be tested.	[14]

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Corn steep liquor	Experinment al study fermentation	Precipitation	48 hours, 50 °C, and pH of 6.5	They obtained 193.50 g/l after 48 hours and recommended that future studies that consider high conversion of sugar into the final product in order to reduce downstream cost.	Precipitation methods which produces more bye products (gypsum) was used and downstream processing was also not carried out.	[13]
not defined	Theoretical Approach/R eview	not defined	not defined	They carried out a review on LA production and highlight its potentials and economic impact.	Downstream processing and purification is a main challenges limiting the cost and viability of LA yield.	[97]
not defined	Theoretical Approach/R eview	not defined	not defined	They reported Production of lactic acid from glycerol via chemical conversion using solid catalyst.	Producing LA form organic solvent which is toxic and non- biodegradability. Solid catalyst is highly cost, its preparation and purification add to the cost of LA.	[98]
citrofortun ella microcarp a fruit waste	Experinment al study fermentation	Precipitation (H ₂ SO ₄)	72 hours, pH 10-11, and temperature range of 80-100 °C.	They investigate the possibility of using the waste from the processing of <i>C</i> . <i>microcarpa</i> fruit waste as substrate in the production of lactic acid by <i>L. plantarum</i> .65 g/l of LA was obtained.	Purification and optimization were not carried out and organic solvent was used which are not friendly to the environment and produced more by- products like calcium carbonate.	[99]
Corn flour	Experinment al study via fermentation	Precipitation	50 °C, 100 rpm, and pH of 6.5.	They investigate the effects of pH, glucoamylase, pullulanase, and invertase addition on the degradation of residua l sugar.	Downstream purification of LA such as precipitation, distillation and membrane separation are not efficient hence the need to look for an alternative.	[100]
not defined	Theoretical Approach/R eview	not defined	not defined	They outline the main problems of LA production to include substrate inhibition, indirect utilization of polymeric sugars, contamination problems, sensitivity to inhibitory compounds released during biomass treatment, decreased lactic acid yield, end products inhibition, and low optical purity of lactic acid.	There is need to look for alternatives method of producing efficient and high yield of LA via eco- friendly and sustainable way.	[101]

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Corn steep liquor and cassava bagasse	Experinment al study via fermentation	Precipitation	50 °C , 48 hours and pH of 5.0	They obtained the LA maximum concentration (31.6 g/L).	Downstream processing of LA was not carried out.	[102]
not defined	Theoretical Approach/R eview	not defined	not defined	They conclude that novel technological developments of lactic acid production to increase yield and decrease over-all cost have become the primary goal.	The uses of novel Deep eutectic solvents as both pre-treatment and extraction solvents can be investigated.	[103]
Agric waste	Experinment al study via fermentation	Filtration and ion exchange and extraction	24 hours, 50 °C, 100 rpm and pH of 7	They carry out LA purification and recovery experiment using double filtration with charcoal and Celite followed by a cation ion exchange column led to the economic 80% recovery of LA.	Filtration required additional process step which add to the cost of LA. ion exchange is very costly. Extraction solvent (ether) used was toxic and showed low distribution coefficients.	[104]
beechwoo d and pine	Experinment al study via fermentation	Precipitation	72 hours, 160 rpm 44 °C, and pH 5.5.	62 g.L ⁻¹ lactic acid representing 41.4% was obtained.	There is need to look for alternatives.	[105]
Whey	Experinment al study via fermentation	Kinetics modelling of LA	37 °C, pH (5.5), and agitation of 200 rpm.	The biomass growth, lactic acid production and lactose utilisation kinetics of lactic acid production from whey by <i>Lactobacillus casei</i> was studied and a maximum productivity of 2.5 gdm ⁻³ .h ⁻¹ was attained.	Other kinetics models such as leudking-piret and logistic model can be investigated and compared.	[106]
not defined	Theoretical review/study	not defined	not defined	a promising technique called emulsion liquid membrane (ELM) along with its current advances is proposed for LA separation.	Scale of this type of membrane is difficult.	[85]
not defined	Experimenta l study	Extraction	55 °C, 2 hours, and 450 rpm.	They develop extractants (N, N-didodecylpyridin- 4-amine) with a higher affinity for carboxylic acids than trioctylamine, and for lactic acid separation and obtained 80% extraction efficiency.	The extractant (<i>N</i> , <i>N</i> -didodecylpyridin-4-amine) are toxic and showed low distribution ratio and it's not recyclable.	[107]
not defined	Experimenta l study	Extraction	not defined	They evaluate the uses of several organic solvents as an extractant for LA purification and obtained a maximum of 77% efficiency.	Organic solvent used which are toxic and non-biodegradable and show low distribution coefficient for LA separation.	[108]

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Food	Experinment	Ultrasonic	37 °C, pH 6.0,	They obtained LA 82 %	Conventional	[109]
waste	al study via	solvent	and at agitation	recovery via this	extraction solvent	L]
hydrolysat	fermentation	extraction	speed of 200	methods.	such as ethyl is toxic,	
e and			rpm.		non-biodegradable,	
bakery			-		non- recyclable shows	
waste					unfavorable	
hydrolysat					distribution	
e					coefficients.	
Cassava	Experinment	Ion	40 °C, 24 hours,	They obtained 70 % LA	Extra filtration steps	[110]
bagasse	al study via	exchange	and pH of 6.0.	recovery via this method.	were required to	
	fermentation	and			complete the process	
		Adsorption			and generate high	
					amount of waste.	
not	Experinment			They obtained extraction	TOA and TOMAC	[111]
defined	al study via	Reactive	27 °C and 102	efficiency of 71.5%	are toxic and showed	
	fermentation	extraction	rpm.	using solvents (TOA and	low distribution ratios	
				TOMAC).	and not recyclable.	
Glucose	Experinment	Precipitation	37 °C, pH =	151.2 g/L was obtained	They did not carry out	[112]
	al study via		6.5,50 rpm, and	as the optimum LA	purification and the	
	fermentation		24 hours.	production.	organic solvent used	
					was toxic.	
Sugarcane	Experinment	Reactive	not defined	They carry out techno-	Other methods of LA	[113]
bagasse	al study via	distillation		economic analysis and	can be evaluated.	
and	fermentation			environmental impact		
leaves				assessment of		
				lignocellulosic lactic acid		
				production.		

Among the several studies carried out with regards to the use of feedstock materials for LA production (with details presented in **Table 5**). Some of the feedstock considered entails Cassava [96-110], sugarcane bagasse [113], Sweet sorghum juice [2], corn steep [93-102], corn flour [101], ground nut shell [95], whey [106], yam peel [1], and food waste [109] where the report for the use of corn cob was found to have shown the highest yield (82 %), while the cassava has shown the least yield with 8.30 %.

The use of sweet sorghum juice, cassava peels, sugarcane bagasse, rice husk, and corn cob, for the production of lactic acid has been proven from the reported research works to be of a high yield confirming the materials to being a good potential resource that aid toward the commercialization of lactic acid in developing nations like Nigeria, where these resource materials are wide disposed randomly within its surroundings as waste for animals to feed on or allowed to just decompose and pollute the environment. It also provides food security as the feedstocks are not sources of food. Although the Nigerian state stands out among agricultural oriented Africa countries, with many lignocellulosics crops such as sugarcane, maize among others, largely growing and cultivated in Nigeria. It is however a serious worrisome decibel for most of these crops to be effectively utilized not only for lactic acid production, but also a consumable food stuff without necessarily hiking the prices and affordability of these crops. Hence the need to strike out a balance between its commercial and economic benefits [114]. From Table 5, kinetic study and detail optimization of lactic acid needs more attention while study on pilot scale plant and techno economic analysis of LA production are also scanty in literature hence these calls for consideration of alternatives methods that will produce LA efficiently and pose no threat to the environment.

Price of pretreatment of materials to a great extent is one of the main limitations towards the development and economic viability of LA production by fermentation [77]. Hence, there is an urgent need for alternative pretreatment methods using solvents that are cost effective and eco- friendly (DESs).

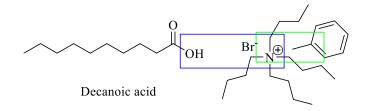
6. Mechanism of DESs as an Extraction Solvent for LA

It has been established in literature that one of the most challenges of DESs application is the illustration of its mechanism for the desire applications. Several authors posited that DESs is more of an art than science in understanding its mechanism for its various applications and full knowledge of its mechanism is still lacking in literature. So far and to the best of our knowledge, there has not reported any reaction mechanism for particular application, Hence, in understanding the mechanism of DESs as an extraction solvent for LA, The mechanism depends on the HBD and HBA of the components of DESs. The functional groups of each components used in the formulation of DESs, the hydrogen bond interaction and electron transfer between the DESs functional group to target a particular functional group in the solute to be extracted. Some characterization techniques such as physical properties of DESs and chemical analysis such as FT-IR, SEM, XRD, TEM, DSC, etc. should be carry out to unveil the interaction between DESs and the target compound, by doing this, it will aid in reviewing the mechanism of DES for extraction. Greatly, to understand the DESs mechanism, a computational approach is required to fully understanding the mechanism of DES application. LA is also a good HBD for formation of DESs; hence, the mechanism is to formulate hydrophobic DESs that will have high affinity for LA from the aqueous solution. Our work is ongoing in the laboratory and in our subsequent publications we attempt to unveil the mechanism behind this novel solvent for it is used in LA extraction. Several authors recently make an attempt to explain the mechanism of DES for extraction. According Abbot et al [23], lignin is the only aromatic biopolymer in lignocellulosic biomass and the Earth's most prevalent renewable aromatic molecule. It is a polymer made of p-coumaryl, coniferyl, and sinapyl alcohols that is heterogeneous. The three monolignols units polymerize in the phenyl rings several times to create the phenyl propanoid units, which are

represented by the letters phydroxyphenyl (H), guaiacyl (G), and syringyl (S), respectively. As a result, lignin has a variety of functional groups available. DES is a synthetic solvent created by combining hydrogen bond acceptor (HBA) with hydrogen bond donor (HBD) [23]. They reported that depending on the nature of the initial components, DES's characteristics can be modified based on the application need. Different DES types have been used in the pretreatment of biomass and the DESs received the greatest research are HBA: polyol and HBA: carboxylic acid. While DES made of polyol shown excellent efficacy in improving the efficiency of enzymatic hydrolysis, whereas the acid-based DES proved successful in lignin extraction [23]. It was reported from the literature that acidic DESs were more capable of fractionating and delignifying materials than basic and neutral DESs. This promotes the investigation of organic acid as a potential replacement for mineral acid in the processing of biomass. Hence, from the earlier finding that revealed acidic DES as a promising lignin extraction solvent. However, the mechanism of DESs extraction depends on functional groups in HBD and HBA of DES, the molar ratio of DES constituents that would lead to better performance in addition to characterization studies on DES-extraction products such as FT-IR, XRD, H-NMR.SEM, TEM, DSC, etc. and the other feasibility studies to further confirm their performance.

The mechanism of DES for extraction hinges on hydrogen bonding and electron transfer. Alkyl groups boost the oxygen's electron density in the acid's OH group by giving electrons. This increases the strength of the hydrogen bond between hydrogen and oxygen, which results in the creation of a weaker acid with weaker acid ionization.

The DES ability to donate protons in solventsolute interactions will therefore increase as the length of the aliphatic chain is reduced. The hydrogen-bond acidity solvatochromic parameter measures this ability. To make lignin extraction easier, a higher value is preferred for dissolving the lignin-carbohydrate complex in lignocellulosic biomass. In terms of extraction, the alkyl ammonium ion is a unique cation that



Tetrabutylammoniumboromide

Figure 5. Mechanism of extraction

successfully creates an aromatic ring complex interaction between the quaternary ammonium ion's electron clouds and the aromatic rings delocalized Π -electron clouds of biomass. The alkyl ammonium ion's in the HBA which is somewhat positively charged H- atoms are naturally surrounded by a Π -electron cloud, which considerably aids in the quaternary ammonium ion's attachment to the aromatic molecule. **Figure 5** depicts a typical mechanism of extraction using DESs.

The creation of a contact Π -aromatic interaction pair that may be more stable than the ion pair between tetra-alkyl quaternary ammonium ions and anionic residue of aqueous solution is facilitated by cation-aromatic interaction. The cation Π -non-covalent relationship between an inorganic cation and the cationic moiety of an organic molecule and the Π -electrons of hydrocarbons like alkenes, alkynes. or aromatics is referred to as a cation-interaction. This interaction is in line with Dougherty and Stauffer's theory, according to which the interaction between charge-quadrupole and charge polarizability is what causes the major binding forces in the complexing of Me_4N^+ (thymol) with lactic. Therefore, it might be said that the interaction between cations and aromatics reflects the extraction mechanism. DES have been used for extraction of fatty acids from food waste, lignin from biomass and metals from waste water hence, it has potential to extract lactic acid from biomass.

7. Prospects and Future of Producing Lactic Acid from Deep Eutectic Solvent

A variety of multipurpose deep eutectic solvents can be prepared with characteristics superior to those reported for conventional organic solvents such as butanol, trioctylamine, methanol, hexane, and ionic liquids (ILs). The deep eutectic solvents are less toxic, more biodegradable, and quicker and easier to prepare, easily recyclable and do not require further purification steps. Furthermore, their unfavourable properties can be overcome by tailoring them, for instance, by changing the nature of the salt or the molar ratio of HBA to HBD, by adding appropriate amount of water if the DESs is highly viscous, by changing temperature or pressure and formation of ternary deep eutectic solvent through combinations of more components to meet a desire target or properties for a particular application like azeotropic extraction.

The existing routes for the production of LA from agricultural residue and food waste could be optimized, with the possibility of taking full advantage of the features and advantages of deep eutectic solvents over conventional organic solvents. The future prospects of the application of DESs for cellulose dissolution and pretreatment of biomass have been established in literature [39-69]. Hence, the feasibility of a LA production via sugar fermentation and purification and in this case, DESs has the potentials to be employ as multifunctional agents as it can be used as pretreatment and extraction solvents [8]. Therefore, there is need to carry out feasibility studies and an investigation into the production of platform bio compounds like lactic acid owing the potentials of its physicochemical characteristics such as biodegradability, less toxicity, nonhighly volatile, cheap, and recyclable and tuneable unlike the conventional solvents that have been utilized in the production of lactic acid. Similarly, DESs ability for cellulose

dissolution boosts further prospects of its use in production of lactic acid. Further survey of literature has unveiled several works that did not pay attention to optimization and kinetics studies of DESs application for delignification, extraction, etc. which are necessary for establishment, commercialization and scale up of pilot plant of such production process like Lactic acid from lignocellulosics matertials. No literature has considered the feasibility of a pilot study involving the use of DESs for extraction and pre-treatment. Moreover, there is no literature currently establishing the techno-economic analysis of the uses of DESs as a substitute for the conventional and ionic liquids that have been used for several applications. Nigeria, is nationally recognized to be highly involved in agricultural production, is rich in feedstocks, especially as waste products both from industrial and domestic uses. Although not quantified reports have emphasized that a high volume of waste is generated globally daily. Food and Fruit wastes have also been identified as a feedstock for lactic acid production [109]. The abundance of this feedstock in Nigeria is due to its enormous consumption daily [115]. Instead of covering the land with these solid wastes, it would instead benefit the country to convert the enormous agricultural residue into a useful resource by producing lactic acid and reducing land pollution. Another feedstock that is much available in Nigeria, is pineapple peel. This is because Nigeria is the seventh largest pineapple producer in the world and the leading producer in Africa [116]. Therefore, it would be advantageous to use the peels disposed of as waste to produce economically useful lactic acid. Interestingly, paper and paper products consist about 35% by weight of municipal solid waste in Nigeria [117]. In addition, a large collections of Irish potato peels, sugarcane bagasse, corn cob, plantain peels, rice husk, banana peel, sweet potato peels, rotten waste tomatoes, and yam peels can largely find in Kano, Zamfara/Plateau, Katsina, Cross River, Kaduna, Bauchi, and Yobe states in Nigeria, according to the report of the Nigeria national beaureu of statistics (NBS) [2017-2019] for agricultural items production and cost.

Despite the existing application of DESs for treatment and conversion into biomass products, yet there are many valuable contingencies for designing more efficient DESs as a result of complexity of biomass. Moreover, the major challenges in producing most bioactive compounds is in the purification stages; hence, the need to develop a solvent that can give high purity and better extraction efficiency of these valuable compounds such as lactic acid. Using food waste like fruit waste or real food waste or even lignocellulosic biomass from agricultural residues where a single or multi-component can be models for production of lactic acid can be explored. Food waste can serve as potential biomass resources from many sources including households. restaurants, agricultural residues and food processing industries. Therefore, there is a investigate the feasibility need to of single-component transforming biomass. wastes, or multi-food waste into lactic acid using deep eutectic solvents. This is because DESs display properties that will enhance efficient production of LA such as high distribution coefficient, non-toxic recycleability and biodegradability and to the best of our knowledge, DESs have not been explored for this purpose.

Finally, employing DESs as solvent for dissolution of lignocellulosics feedstocks and further as extraction solvent for LA production could be a major step towards building an efficient and sustainable LA purification process since DESs composed of components which are simple or naturally occurring can be tuned, design, innovative, and suitable for extraction of LA and several other applications such as protein synthesis, peptides, and so on.

8. Conclusion

This paper reviews the potential application of deep eutectic solvents for lactic acid production where DESs could be use as both pretreatment and extraction solvents as an alternative to conventional organic solvent and ionic liquids due to low yield, impure LA, low distribution coefficient, high cost of solvents, and non recycleability of the solvents associated with the current conventional methods currently been explore in the LA production. Several techniques for separation and purification have been suggested in literature, the processes are not efficient while some are not environmentally friendly. Also, the common method currently applied uses precipitation by application of calcium hydroxide where the recovery process is carried out using excess sulphuric acid which generates huge amounts of Calcium sulphate as waste to the environment. Lignocellulosics materials as feedstock for LA production look desirable alternatives because they do not contest with food crops, very cheap, renewable, and abundantly available. One of the ways to reduce the cost of lactic acid is to source for low cost, cheap, renewable, and also materials that have properties such as high yield, negligible formation of by-products, higher productivity, and low impurity. DESs offer numerous social (acceptability sustainability), and environmental and economic advantages hence, more research is required to explore the potentials of this unique and novel DESs especially for production of platform chemicals like lactic acid. Finally, to increase yield and purity of lactic acid, green solvents as substitutes for traditional organic solvents (VOCs) and ionic liquids should be sought for. Lastly, novel pretreatment methods without or with minimal generation of hazardous byproducts and innovative LAB strains have to be developed to assure effective LA production. The DESs properties could offer several advantages such as better pretreatment solvents, may give higher extraction efficiency recvclable easilv compared and with conventional organic solvents and ionic liquids. Hence, there is need to carry out feasibility study of this novel solvents for its use in lactic acid production via fermentation.

Conflict of interest

The authors declare no conflict of interest. Acknowledgment

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