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DETERMINATION OF SELECTED ELEMENTS IN CATALYTIC CONVERTERS USING ICP-MS AND MICROWAVE DIGESTION

Weronika Kieres
Unimetal Recycling Sp. z o.o.
21 Tuwima Str., 32-540 Trzebinia, Poland

Grzegorz Palka
Unimetal Recycling Sp. z o.o.
21 Tuwima Str., 32-540 Trzebinia, Poland

Karolina Łuczak-Zelek
Unimetal Recycling Sp. z o.o.
21 Tuwima Str., 32-540 Trzebinia, Poland

Monika Partyka*
Unimetal Recycling Sp. z o.o.
21 Tuwima Str., 32-540 Trzebinia, Poland, mpartyka@unilab.biz
https://orcid.org/0000-0002-8006-0585

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Abstract
Fuels combustion, polluting the atmosphere is a side effect of an engines' work. Increasing ecological awareness has led to constant pursuit of disposing harmful substances properly. Catalytic converters (car catalysts), containing precious metals from the platinum group, including palladium, platinum and rhodium, have been commonly adopted for this purpose. These critical elements can be found in many raw materials used frequently throughout the economy. Therefore, it is economically viable to retrieve these elements from, among the others, spent catalysts, so they can be reused to manufacture new converters. In order to determine a possible cost of spent car catalyst, it is essential to use the analytical techniques to determine elemental content in any given sample. X-ray fluorescence spectroscopy (XRF) is an example of such a technique. It is nevertheless advisable to use a complementary procedure to confirm any results obtained. A cross-verification technique was developed using inductively coupled plasma mass spectrometry (ICP-MS). This procedure was verified using comparative studies, which confirmed its usefulness and correctness.

Keywords
ICP-MS, car catalyst, catalytic converter, microwave digestion, circular economy

Introduction

Combustion engines are the main source of propulsion of not only cars, but also trucks, buses, and other types of machines. During their duty cycle, fuel is burnt and, as a side effect, harmful substances are emitted into the atmosphere. Due to the increase in ecological awareness and progress as a society, attempts to neutralise the polluting compounds have been initiated, leading to the introduction of catalytic converters, known as catalysts [1,2]

One of the components forming ceramic catalysts is a ceramic monolith, a ceramic core block usually with a honeycomb structure. This structure contains tubules covered with precious metals – palladium, platinum and rhodium that are responsible for the catalytic function, which reduces harmful emissions.

Unimetal Recycling Sp. z o. o. is an enterprise whose objective is retrieving precious metals from used catalysts, fitting into pro-ecological activities and participating in creating the circular economy. Precious metals from the platinum group (PGM) are critical raw materials for the economy [3]. Implemented in many branches, they are however difficult to obtain from nature. That is why their retrieval and recycling is essential both from the economic and environmental point of view.

During normal operation, in cleaning vehicle emissions, the initial content of precious metals in catalysts reduces over time. The final amount depends on many factors such as for example, the type of combusted fuel, the

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vehicle's age, and even driving style. This creates a vital demand to determine the amount of the targeted elements remains. The prospective income and ability to further process the catalyst batch all depend on precise and accurate measurement of the palladium, platinum, and rhodium levels. Since there are no norms for elemental content in spent catalysts, the most popular technique is XRF (X-ray fluorescence spectroscopy) which is simple and easy to operate [4–6] . In performing routine tests, there is no need for specialised personnel. Only the device calibration needs the appropriate equipment and service. According to literature data, handheld XRF offers the user several essential advantages – analysis can be done in the field in a matter of seconds, instead of in a lab with wet chemistry and a highly skilled analytical professional, significantly cutting the cost of accurate analysis of precious metals concentration in catalytic converter scrap [7,8]. XRF has many advantages yet it is often necessary to confirm any results with an alternate method established on different physical and chemical principles. In our laboratory a new measurement method has been developed, allowing for cross-validation of measurement of precious metals concentration obtained using XRF technique. The developed measurement method uses inductively coupled plasma mass spectrometry (ICP-MS) technique, with samples being prepared by microwave digestion.

Methods

In this study, the chosen material, monolith from spent car catalysts, was obtained from individual and mass providers (e.g., vehicle disassembly stations, service stations, collection points) in compliance with all rules of conduct provided by the relevant laws. *Unimetal Recycling Sp. z. o. o.* performed the processes of separating the monolith from other catalyst parts and averaging and homogenising it. Homogeneous material testing was carried out with the ICP-MS spectrometer NexION2000P (*Perkin Elmer*) and the microwave mineraliser Titan MPS Microwave Sample Preparation System (*Perkin Elmer*). Digestion was carried out using a variety of acids (hydrochloric acid for trace analysis, *Honeywell Fluka* and nitric acid, *VWR AnalaR Normapur*). Calibration solutions, for standard curve determination and validation of the tested method, were prepared using commercially available standard solutions (palladium, platinum and rhodium concentration 1000mg/L, *Chem-Lab*). Suitability of the equipment was tested with NexION Setup Solution (*Perkin Elmer*). Additionally, verifying the developed sample preparation method and final analyses were performed using certified reference materials – Used Auto Catalyst FLX-CRM 132 and FLX-CRM 133 (*Fluxana GmbH & Co. KG*). To confirm the advantage of the developed methodology, parallel tests were performed. Results of which were compared with the results obtained using the XRF spectrometer (*GoldXpert, Olympus*) and ICP technique (analysis by the monolith recipient). The flow chart in Fig. 1 illustrates the procedure.

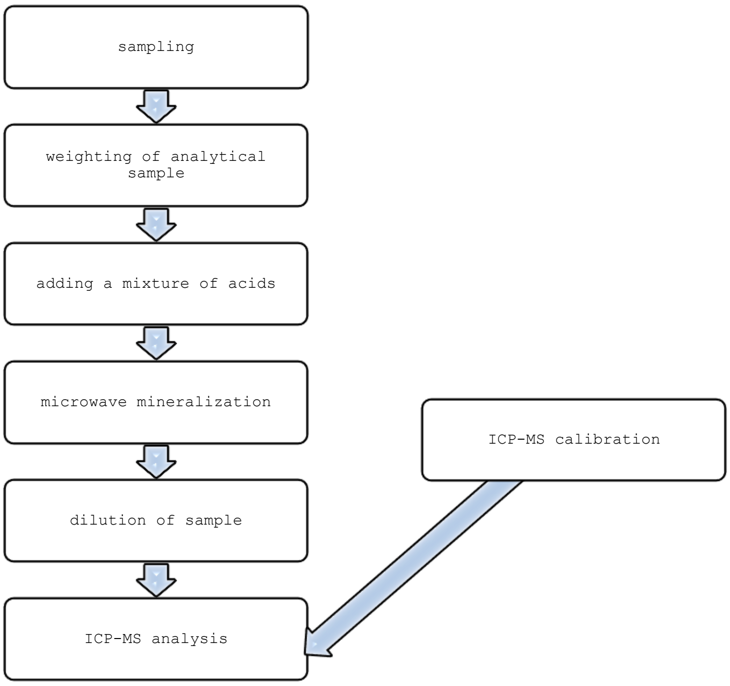

Fig. 1. Measurement procedure steps. *Source: Author's.*

Results and discussion

The suitability of ICP-MS was tested against a corresponding solution used for optimisation of the system. The manufacturer specifies the conditions, which ensure the device having been properly adjusted and ready to work, enabling recording of reliable measurements. In this case, they are respectively:

- Be 9.0122 > 2000 [cps],
- In 114.904 > 40000 [cps],
- CeO/Ce ≤ 2.5%,
- $Ce^{++}/Ce \leq 3\%$.

The evaluation of the calibration curves' linearity was done based on injections of the standard solutions prepared in inorganic solvent (diluted acid) at concentrations presented in Table 1. These solutions were each analysed three times. A range of element concentrations was determined in the samples of 200-3000 ppm for palladium, 20-2000 ppm for platinum, and 10-500 ppm for rhodium, respectively. The scope of determination was selected based on own experience and literature data and indicates that the total content of these metals is up to 2000 ppm in the ceramic base. In some works, it is mentioned that car catalytic converter contains typically around 800 - 1000 ppm of platinum, 400 - 1000 ppm of palladium and 60 - 150 ppm of rhodium [9–13].

Table 1. Concentrations of calibration solutions. *Source: Author's.*

Calibration level	**Palladium, c [µg/L]**	**Platinum, c [µg/L]**	**Rhodium, c [µg/L]**
1	10	1,0	0,5
2	25	10	1,0
3	50	25	5,0
4	100	50	10
5	150	100	25

Calculations were performed to ascertain the average peak areas, relative standard deviations (RSD) and calibration curve equations. Coefficients of determination (r^2) and linear ranges were determined for each element analysed. Achieved linear coefficients of correlation and determination for each element are presented in Table 2 whereas calibration curves are found in Fig. 2.

Table 2. Correlation parameters for calibration curves of each element. *Source: Author's.*

	Palladium	**Platinum**	**Rhodium**
R	0,9990	0,9999	0,9999
r^2	0,9979	0,9998	0,9998

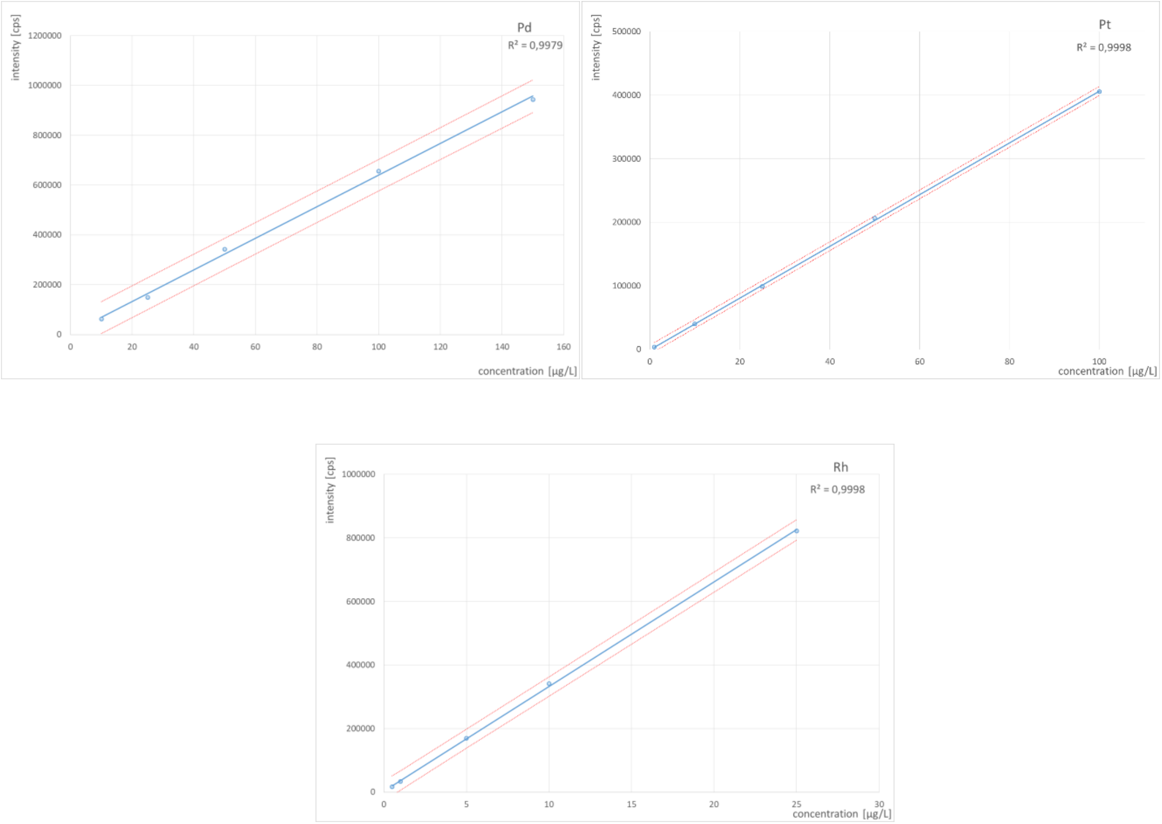

Fig. 2. Calibration curves with confidence intervals. *Source: Author's.*

Repeatability of the findings was investigated by testing the calibration solutions (n=3). Relative standard deviation (RSD) did not exceed 2% for palladium and platinum and 3% for rhodium. Accuracy was verified on a sample without any precious metals, spiked with calibration solutions. Recovery resulted in 94% for palladium and platinum, 91% for rhodium. In addition, the procedure was verified with certified reference materials (FLX-CRM 132 and FLX-CRM 133). The recovery results did not exceed 80 - 120%. Furthermore, standard uncertainty was estimated at less than 10% for palladium and platinum and less than 12% for rhodium. The validation confirmed the adequacy of the newly developed procedure in analysing platinum group elements in ceramic monolith, derived from used catalysts, with accuracy and precision.

The study was followed by determining if the procedure is complementary to standard XRF analysis and ICP method used by homogenised monolith recipients. For this purpose, 20 powder samples were examined with XRF and ICP-MS. The obtained results were compared against the recipients' results during the material verifying process. A strong correlation was found between both ICP-MS results in reference to XRF and recipients' results (Fig.3.).

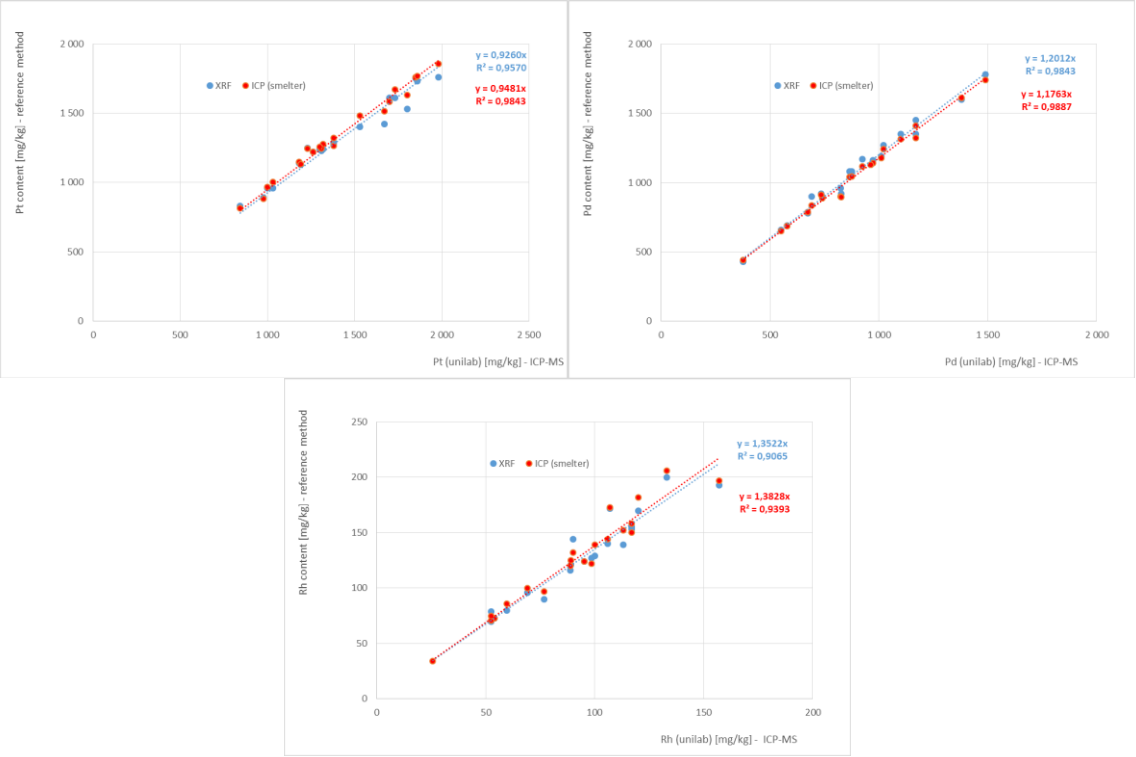

Fig. 3. Correlation between results obtained from the newly developed method, standard XRF procedure and acquired by the material recipient. *Source: Author's.*

For palladium and platinum, the coefficient of determination value was over 0.95, which implies a strong correlation. Slightly weaker results were received for rhodium. However, the r^2 value was over 0.90 for all comparisons. The obtained results confirm also the mentioned above literature data, regarding the content of precious elements in spent car catalysts [9-13] – platinum content was between 800 - 1800 ppm (average 1300 ppm), palladium – 400 - 1700 ppm (average 1000 ppm), and rhodium 30 - 200 ppm (average 130 ppm).

Impact

This study demonstrates the effectiveness of an innovative application of a modern analytical technique, complementary to XRF. The developed procedure produced adequate precision and accuracy with relatively small uncertainty, making it a good complimentary method to XRF. The research results expand current scientific knowledge, thereby raising awareness of possible analytical techniques to determine precious elements (Pd, Pt and Rh) from catalytic converters. The PGM loading in ceramic honeycomb can be determined by ICP-MS technique as confirmatory technique, according to customer's demand. It could be a big benefit for the customer - having a result from another analytical method. Important is, that – based on literature data - the ICP-MS showed the lowest detection limit and less spectral interference than the XRF technique [14].
This study also promotes the circular economy, demonstrating the impact of *Unimetal Recycling Sp. z o.o.* operations in this space. It is a good link between the industry and R&D processes. High demand requires high quality of quantification of the retrieved elements. As previously mentioned, PGM are crucial for the economy. Spent automotive catalysts are a valuable source of important metals such as platinum, palladium and rhodium. They have a high recyclability, therefore it is more convenient to reuse them than get the ores from all around the world. In South African and Russian mining concentration of Pt, Pd, Rh deposits make less than 0,001% per ore [15] (it can be lower depending on the dilution with rocks in the mining process) in car catalyst it could be more. It is the reason why is so critical to the precious metals market to recover the elements and the obtained method makes the determination of concentration in materials easier and allows to have a parallel to XRF (confirmatory) technique.
Another benefit for market and environment would be the application of PGM. Not only automotive industry

is eager to use them. Due to its high temperature stability, melting point and corrosion resistance rhodium's properties are key to glass fibre production. Palladium is exploited in electronic components plating, making it more durable and effective than gold. It is also safe and efficient medium for storing hydrogen and a purifier. Platinum's 40% of the overall use is jewellery. It also plays an important role in medical applications, being biologically compatible. In compounds, it can inhibit the cancerous cells from growing [16]. Variety of industries are using the platinum group metals and the demand is growing. Considering the bigger picture, developed method shows potential and is a contribution to the industry and economy.

Conclusions

XRF technique is a fast, economical, and easy to operate analytical technique, which marks the elemental content in ceramic monolith derived from spent car catalytic converters. There is a major drawback to it, appearing in a high RSD value in results. That is why it is often necessary to implement a complimentary technique allowing achieving results with higher accuracy. One possible solution is ICP-MS, verified by the monolith recipient. The method developed produces outcomes with high precision and accuracy. The obtained results allow evaluating the used catalyst converter, for pricing in trade settlements and classification in terms of the possibility to retrieve precious metals.

Conflict of interest

There are no conflicts to declare.

Acknowledgments

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THE ROLE OF BROWNING ENZYMES IN CHERRIES

Kristyna Ruzickova
Laboratory for Separation Processes and Product Design, Faculty of Chemistry and Chemical Engineering
University of Maribor
17 Smetanova str., SI-2000 Maribor, Slovenia

Maja Leitgeb*
Laboratory for Separation Processes and Product Design, Faculty of Chemistry and Chemical Engineering
University of Maribor
17 Smetanova str., SI-2000 Maribor, Slovenia; maja.leitgeb@um.si
https://orcid.org/0000-0001-9303-686X

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Abstract
Cherries contain significant amounts of important nutrients and bioactive food components including fibre, polyphenols, carotenoids, vitamin C, potassium. They are also good source of tryptophan, serotonin, and melatonin. Beside the fact that cherries are considered as an excellent source of numerous nutrients and they also present a low caloric content. These facts lead to their increasing popularity in the human diet. Numerous studies suggest that their regular consumption has a positive effect on health and the well-being of individuals. Another bioactive food components found in cherries are enzymes. The interest in research about enzymes in cherries is not so significant as for other compounds like polyphenols or vitamins. However, number of studies were carried out to characterise enzymes and their function in cherries especially with relation to extending their shelf life. The aim of this work is to give a brief overview of latest research on browning enzymes, softening enzymes and glutathione S-transferase.

Keywords
cherry fruit, browning enzymes, softening enzymes, glutathione S-transferase

Introduction

Cherry fruit is a nutrient dense food with low caloric content. There are more than a hundred cultivars of cherries, which are grouped into two major types: sweet and tart cherries. Both types are grown in North America and in temperate regions of Europe and Asia. Cherries do not contain fat and cholesterol and represent low caloric fruit. They contain many essential minerals such as fibre, vitamin A, vitamin C, iron, calcium, proteins as well as abundant potassium. Red cherries also contain melatonin, which helps to protect against harmful toxins. Another bioactive components present in cherries are phenolics. These compounds can act as a free radical scavenger. They reduce reactive oxygen species, such as hydrogen peroxide and superoxide anion. This is very important because reactive oxygen species are associated with chronic diseases such as cardiovascular disease and cancer. Furthermore, due to its antioxidant properties, cherry fruit has many benefits such as prevention of some types of cancer, reduction of inflammation, prevention of gout and removal of muscle pain. With all mentioned advantages cherries get more popular among consumers [1,2].

One of the main issues with cherry production and fruit production in general is browning, which alters fruit colours, flavours, texture, and thus lowers its marketing value. The browning process can be caused by either enzymatic or non-enzymatic biochemical reactions. Two enzymes involved in the browning process are polyphenol oxidase (PPO) and peroxidase (POD). Several studies were carried out to find a way of treating cherries that would extend their shelf life by inhibition PPO and POD enzymatic activity for example by using chitosan coating or modified atmosphere packaging [3].

This paper gives a brief overview on studies concerning PPO and POD isolation, purification, enzymatic activity during maturation and storage, as well as inhibition of these enzymes by mentioned treatments. Furthermore, research on other enzymes present in cherries such as softening enzymes and glutathionine S- transferase (GST) is discussed.

Cherries

Sweet cherry (*Prunus avium, L.*) and tart cherry (*Prunus cerasus L.*) are the two most important cherry species

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commercially. Both species are native to Southeast Europe and Western Asia. Sweet cherries are grouped into two major types. Heart-type cherries, which are ovoid or heart-shaped and have relatively soft flesh, mostly ripening early. Bigarreau type is more commercially important, the fruit is firmer and crisp-fleshed and ripe mid to late season. Eastern Europe, Slovenia, Hungary, and Romania are large producers of tart cherry, while sweet cherry production is concentrated in Western Europe, Italy, Switzerland, France, and Spain. Worldwide the biggest producers of both sweet and tart cherries are Turkey, the United States, Iran, and Russia. Nutrients and phytochemicals can be found in both, sweet and sour cherries. They have low caloric content, as well (63.0 kcal per 100 g for sweet cherry and 50.0 kcal per 100 g for sour cherry) [4].

Fruit chemistry

The best indicators of quality of both types of cherries are soluble solids and fruit colour. Typically, high quality tart cherries have minimum 15 % of soluble solids and sweet cherries have at least 20 % (Table 1) [4].

Titratable acidity (TA) is another attribute, which plays an important role in the acceptability by consumers. It is highly cultivar-dependent parameter. Cherries are considered as slightly acidic fruit with the pH values of sweet cherries ranging from 3.7 to 4.2 and sour cherries ranging from pH 3.1 to 3.6. Significant differences between sweet and sour cherry and among cultivars in TA were observed. One of the main analytical measures of fruit quality is maturity index (TSS/TA ratio), which influences the perception of sweetness and flavour. With the increase of TSS/TA ratio of cherry fruits the consumer perception of sweetness rises, too. The sweet cherry has lower acidity level resulting in higher TSS/TA ratios. Important factors for sensory quality are aroma and flavour, although the contributing compounds represent only 0.001–0.01% of the fruit's fresh weight (FW). Both, free volatile compounds and glycosidically bound aromatic compounds contribute to aroma of cherries. In first mentioned group more than 100 compounds have been identified with hexanal and benzaldehyde as one of the main compounds. Alcohols represent second largest group following by acids, esters, monoterpenes, sesquiterpenes and diterpenes [5].

Table 1. Comparison of characteristic factors in sweet and tart cherries in 100g edible portion. *Source: [5].*

Component	Sweet cherry	Tart cherry
Soluble solids	20 %	15 %
pH	3.7-4.2	3.1-3.6
TA (malic acid)	0.7-1.2 g	1.4-2.9 g
TSS/TA	19.0-40.0	5.8-15.8

Nutritional composition

The main component of cherries is water with its content of 80-83 % in sweet and 81-88 % in tart cherries (Table 2). The most abundant macronutrients in cherries are carbohydrates. Their amount range from 12.2 to 17.0 g per 100 g edible portion for sweet cherry and the average value for tart cherry is 12.2 g per 100 g edible portion. The protein content is between 0.8 and 1.4 g per 100 g edible portion for sweet cherry and below 1.0 g per 100 g edible portion for tart cherry. The main sugars are glucose, fructose, and sorbitol. Regarding organic acids, the malic acid accounts for 98% of the total organic acid content. The main mineral in cherry is potassium. Other minerals observed in cherries in higher amount are calcium, phosphorus, magnesium, and sodium. Cherries contain significant amounts of vitamins especially vitamin C, vitamin E and vitamin K. Sour cherries have higher content of vitamin A than sweet cherries [5].

Table 2. Comparison of nutritional composition in sweet and tart cherries in 100g edible portion. *Source: [5].*

Component	Sweet cherry	Tart cherry
Soluble solids	20 %	15 %
pH	3.7-4.2	3.1-3.6
TA (malic acid)	0.7-1.2 g	1.4-2.9 g
TSS/TA	19.0-40.0	5.8-15.8
Water	80-83 %	81-88 %
Carbohydrates	12.2 -17.7 g	12.2
Protein content	0.8-1.4 g	<1.0 g
Potassium	260 mg	200 mg
Vitamin A	3.0 mg	64.0 mg

Phytochemical composition and antioxidant activity

Sweet cherries contain many phytochemical compounds. The vast of majority are carotenoids, mostly β-carotene, lutein, and zeaxanthin. Another important group of phytochemicals are polyphenols which contribute to colour, taste, aroma, and flavour of cherries and flavonoids. Those compounds take place in antioxidative defence of plants against biotic and abiotic stresses for example high or low temperatures, drought, alkalinity, salinity, UV stress and pathogen attack. The skin of cherry fruits contains the highest content of total polyphenolic compounds, followed by the flesh and the pit. Recent research suggests contribution of polyphenols in the prevention of cardiovascular diseases, cancers, diabetes, insomnia, obesity, and osteoporosis. Another widely abundant type of aromatic secondary plant metabolites are phenolic acids. They affect food quality and organoleptic properties, and are divided into two subgroups; the hydroxybenzoic and the hydoxycinnamic acids. Flavonoids are also present in cherries including anthoxanthins (flavones and flavonols), flavanones, flavanonols, flavans and anthocyanidins. The common anthocyanidins, that give the attractive colour of cherries, are cyanidin, pelargonidin, peonidin, delphinidin, petunidin and malvidin. Flavonols are very important bioactive compounds, crucial for human health. Six flavonols have been quantified in sweet cherry fruit with quercetin being the main one. Cherries contain also indolamine melatonin (MLT), which is an endogenous hormone. The main function of MLT in mammals is regulation of the sleep–wake cycle, but MLT is also potent free-radical scavenger and a broad-spectrum antioxidant [5].

Enzymes in cherries

There are several enzymes found in cherries. This chapter gives brief overview on research about the most important ones such as enzyme PPO and POD which contribute to enzymatic browning in fruit, glutathionine-S-transferase (GST) which acts as detoxification enzyme protecting cellular macromolecules from attack by reactive electrophiles and enzymes that are responsible for fruit softening during maturation and storage.

Enzymatic browning

Enzymatic browning in fruit or vegetable occurs during handling, storage, and processing. It negatively influences the sensory properties and marketability of the product and decreases the nutritional qualities due to associated changes in colour, flavour, and softening. Approximately 50% losses in fruit occur because of enzymatic browning, which is catalysed by PPO and POD [6].

In the presence of molecular oxygen, PPO catalyses the o-hydroxylation of monophenols to o-diphenols (monophenolase activity) and oxidation of the o-diphenols to o-quinones (diphenolase activity), which polymerise into undesirable brown, red and black pigments. These pigments then affect nutritional value in fruit products. PPO is a copper containing enzyme and it is widely abundant in the plant and animal kingdoms. In plants, PPO is present in chloroplasts and its phenolic substrates are mostly located in the vacuoles. If the cell is damaged, the enzyme can be exposed to substrates which leads to rapid oxidation of phenols. PPOs occur in isoforms which were detected for example in apple, banana grape, kiwifruit, lettuce, mushroom, peach, pineapple, potato, spinach, strawberry, and sweet potato. These isoforms differ in their physical, chemical, or enzymatic properties such as electrophoretic mobility, temperature and pH optimum, substrate specificity and pI. Another enzyme involved in enzymatic browning is POD. It is a dicopper-containing enzyme which is found in plants, microbes, and animals. It can reduce diphenols and this enzyme is also involved in lignin production. POD activity is limited by the absence of electron compounds such as superoxide radicals, hydrogen peroxide and lipid peroxides, however it was reported that the enzyme catalyses the browning process of different fruits and vegetables. To extend a shelf life of a fruit or a vegetable, it is necessary to understand the PPO and POD activity and to determine their characteristics to inhibit or control their activity [6,7]

Isolation and Characterization of PPO from White Cherry Fruit

PPO from white cherry fruit was extracted and purified through $(NH_4)_2SO_4$ precipitation, dialysis, and ion exchange chromatography. Using Toyopearl 650 M column the enzyme showed two peaks with PPO activity, which referred to isoenzyme A and isoenzyme B (Table 3). The isoenzymes were further characterised to find pH optima, temperature optima and affinity for catechol [6].

Table 3. Values of absorbance and white cherry PPO activity on Toyopearl 650 M at the peak. *Source:[6].*

Isoenzyme	**Absorbance (280 nm)**	**PPO activity (units)**
Isoenzyme A	3,6	10,000
Isoenzyme B	0,7	10,000

Extraction and purification

Due to the fact, that some PPOs are membrane-bound, detergents are required to solubilize the enzyme. Phenolic compounds interfere with purification of proteins from plants by cross-linked proteins with hydrogen bonds and covalent interactions. Furthermore, homogenization of the plant tissues initiates enzymatic browning which leads into formation of quinones, that may form irreversible covalent linkages. Phenol-absorbing polymers (polyethylene glycol) and reducing agents (ascorbic acid) are commonly applied to overcome these problems [6]. The frozen berries were deseeded, and the pulps were homogenized in cold acetone containing polyethylene glycol. A filter paper was used for slurry vacuum filtration and the residue was re-extracted with cold acetone. This procedure was repeated until a white powder was obtained and then it was dried overnight at room temperature and stored. Acetone powder was homogenized in phosphate buffer containing ascorbic acid, detergents, and other chemicals, stirred and centrifuged. The resulting supernatant was mixed with ammonium sulphate to precipitate and centrifuged again. A small amount of 10 mM phosphate buffer was used to dissolve the precipitate and dialyze overnight in the same buffer. The dialysate was analysed by ion exchange chromatography and PPO activity was monitored using catechol as substrate [6].

Changes in the Chemical Content and Polyphenol Oxidase Activity during Development and Ripening of Cherry Laurel Fruits

Changes in the PPO activity and in the content of other chemicals during the development and ripening of cherry laurel fruits were investigated (Fig.1). Spectrophotometry was used to analyse PPO activity in the fruits harvested every week from the beginning of June to the mid July. It was observed that PPO activity and phenolic content gradually increased during the development of the fruits but decreased in the stage of ripening [8].

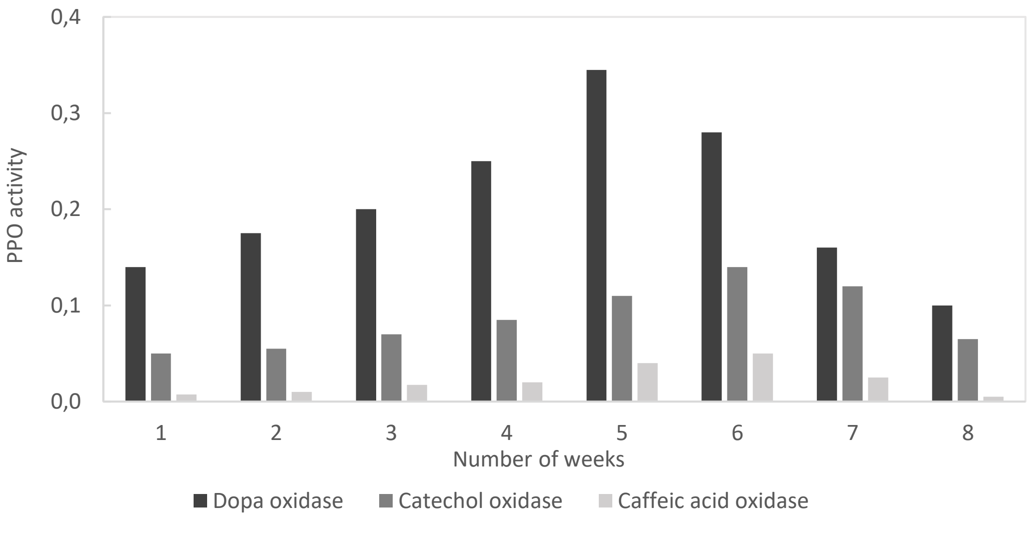

Fig. 1. Changes in the PPO activity during the development and ripening of cherry laurel.
Source: [8].

Polyacrylamide gel electrophoresis was used for further analysis and two isoenzyme bands of PPO were detected. The activities of both isoenzymes increased in the fifth and sixth week, then they decreased in the seventh and eighth week of ripening. The number of PPO isoenzymes did not change during the development and ripening of the fruits [8].

Responses of physiology and quality of sweet cherry fruit to different atmospheres in storage

The storage life of cherries is relatively short. They soften and darken during storage which is unattractive for consumers. Several studies were carried out to find a way of treating cherries that would extend their shelf life. Sweet cherry fruit was stored in modified atmosphere packaging (MAP) and controlled atmospheres (CA) of 5% O_2 plus 10% CO_2; or 70% O_2 plus 0% CO_2 at 1 °C. The effects of different O_2 and CO_2 concentrations on physiological properties, quality attributes and storability during storage periods of 60 days were determined. The inhibition of PPO (Fig. 2) and POD (Fig. 3) and content of malondialdehyde (MDA; the content of MDA indicates lipid peroxidation resulting from oxidative stress) (Fig. 4) were analysed using spectrophotometry and enzymatic activities were defined as an increase in one absorbance unit per minute. It was observed that CA with 5% O_2 and 10% CO_2 more significantly inhibited PPO and POD enzymatic activities and reduced MDA content. Furthermore, more effective was prevented flesh browning, decreased fruit decay, and extended storage life of sweet cherry fruit than did other treatments [9].

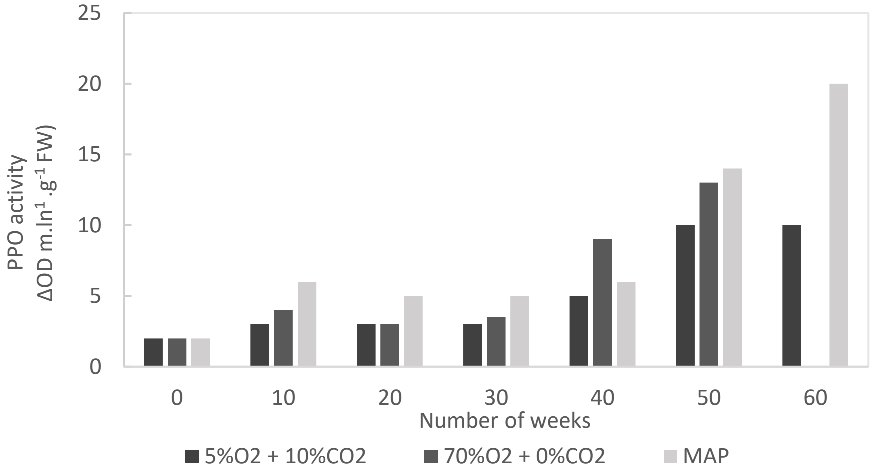

Fig. 2. Changes in PPO activity of sweet cherries stored in different atmospheres at 1 °C during storage periods.
Source: [9].

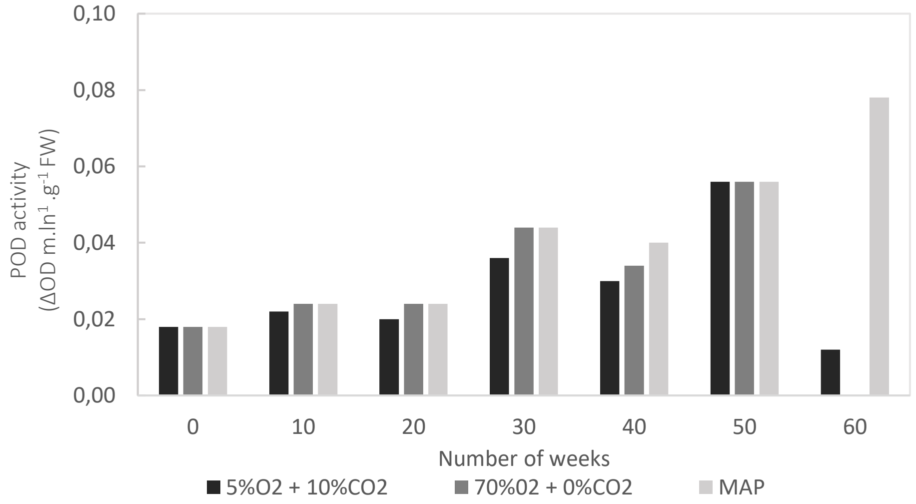

Fig. 3. Changes in POD activity of sweet cherries stored in different atmospheres at 1 °C during storage periods.
Source:[9].

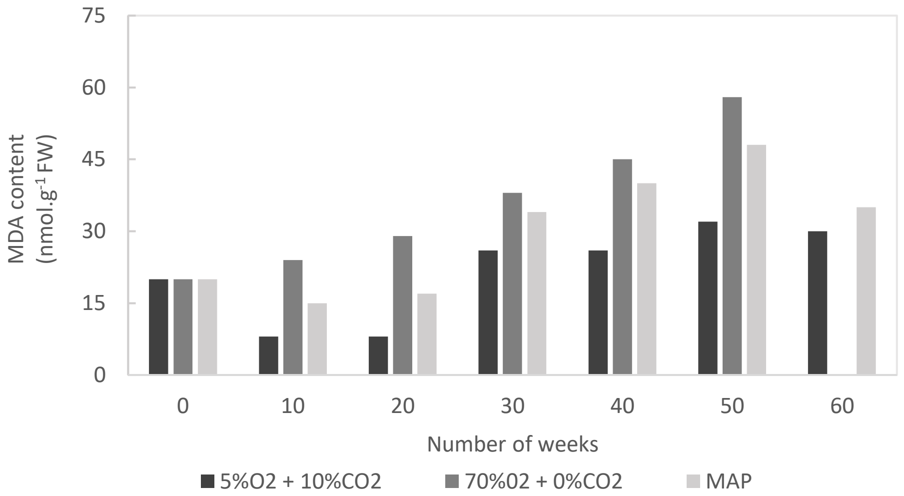

Fig. 4. Changes in MDA content of sweet cherries stored indifferent atmospheres at 1 °C during storage periods. *Source [9].*

The effect of CO_2 concentration on sweet cherry preservation in modified atmosphere packaging

Another study on using different atmospheres for storage of cherry fruits was carried out. Cherries were stored in concentrations of CO_2 at 0%, 5%, 10%, 15%, 20% and 25% (concentration of O_2 was 5% and the rest was filled with N_2). The quality change of sweet cherries was evaluated approximately from –1 to +1 °C and from 80 to 85% relative humidity. Deterioration of sweet cherries was inhibited by all air treatments. The most significant inhibition of reduction of soluble solids and vitamin C and reduction of the PPO and POD activities was obtained in 10% CO_2 group. This treatment reduced rotting rate and maintained firmness, nutrition, and taste of the fruit after 120 days of storage and thus this CO_2 concentration can be used as suitable gas storage conditions of sweet cherries in modified atmosphere packaging [10].

Influence of postharvest chitosan treatment on enzymatic browning and antioxidant enzyme activity in sweet cherry fruit

A study focusing on extending shelf life of cherry used chitosan as a treatment for cherries. The effect of chitosan fruit coating on enzymatic browning and antioxidant enzyme activity in three sweet cherry cultivars was evaluated. Cherries were dipped into 0.5% chitosan solution, stored at 2°C for 14 days (Fig. 5) and sampled at harvest, 7 and 14 days of cold storage followed by storage at 24 °C for 3 days (Fig. 6) to evaluate the shelf life of the fruit. Cherries were homogenized in sodium phosphate buffer containing polyvinylpyrrolidone (PVPP). Crude enzyme extract was incubated with a buffered substrate (catechol in sodium phosphate buffer) and monitored by measuring the increase in absorbance. Cherries dipped in distilled water were used as a control. The treatment inhibited PPO and POD activities and as a result flesh-browning was prevented. Therefore, storage life of sweet cherry fruit was extended [11].

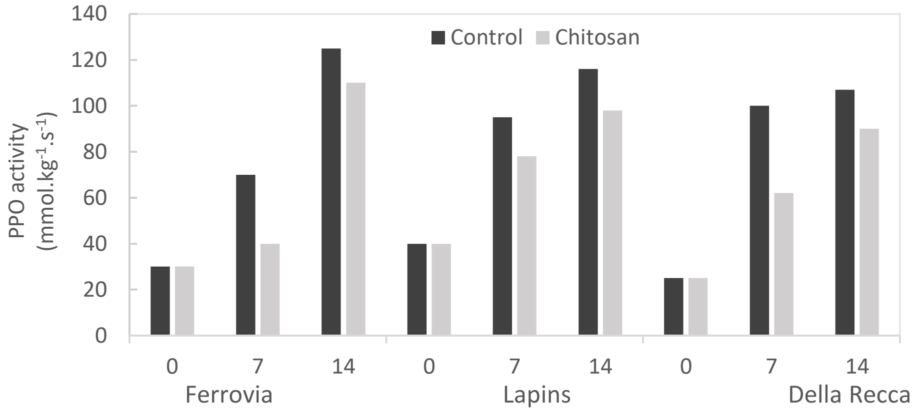

Fig. 5. PPO activity of the three sweet cherry cultivars at harvest (0), after 7 and 14 days of cold storage on chitosan-coated (chitosan) and uncoated fruit (control). *Source: [11].*

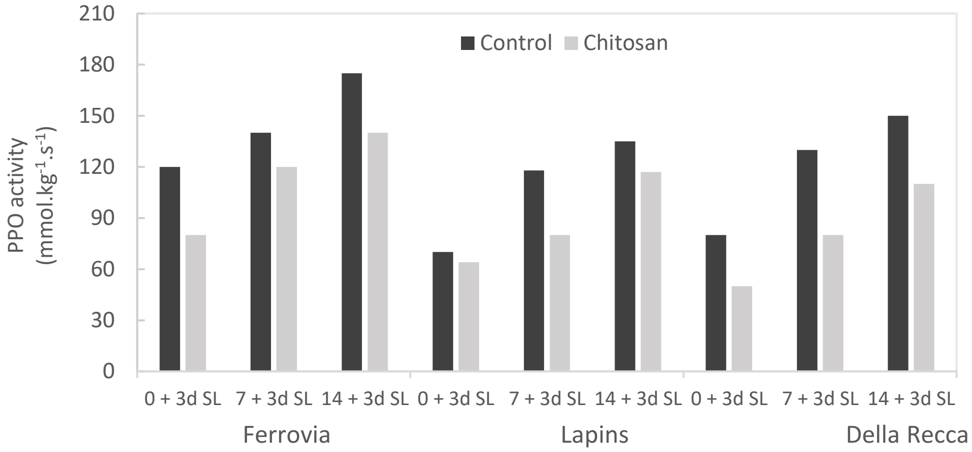

Fig. 6. PPO activity on the three sweet cherry cultivars at harvest after 3 days of shelf life on chitosan-coated (chitosan) and uncoated fruit (control). *Source: [11].*

Effect of β-aminobutyric acid on cell wall modification and senescence in sweet cherry during storage at 20 °C.
An experiment investigated how the postharvest β-aminobutyric acid (BABA) treatment affects fruit firmness, pectin degrading enzymes, cell wall constituents and microstructural alterations of pericarp in sweet cherry fruit. The results showed that BABA treatment slowed down fruit senescence and softening, probably due to depressed membrane permeability and malondialdehyde content. Activities of polygalacturonase (PG) and pectinmethylesterase were significantly decreased by BABA treatment. Furthermore, the treatment enhanced cell wall polysaccharides content and maintained subepidermal cell structure in sweet cherry.
PG activity was measured using spectrophotometry and pectin methyl esterase (PME) activity using acid-base titration. BABA treatment inhibited PG activity (Fig. 7) after 3 days of storage and PME activity after 2 days of storage (Fig. 8). On the 5th day, activity of PME was 25% lower than activity in control fruit [12].

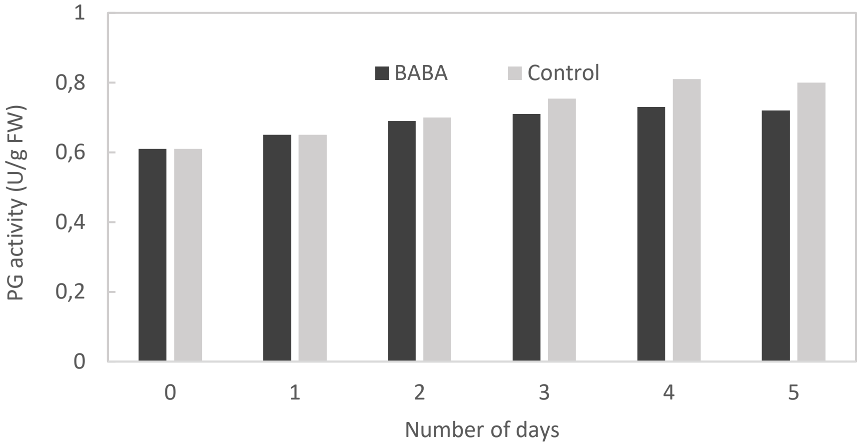

Fig. 7. Effect of BABA treatment on PG activity in sweet cherry fruit during storage at 20 °C. *Source:*[12]

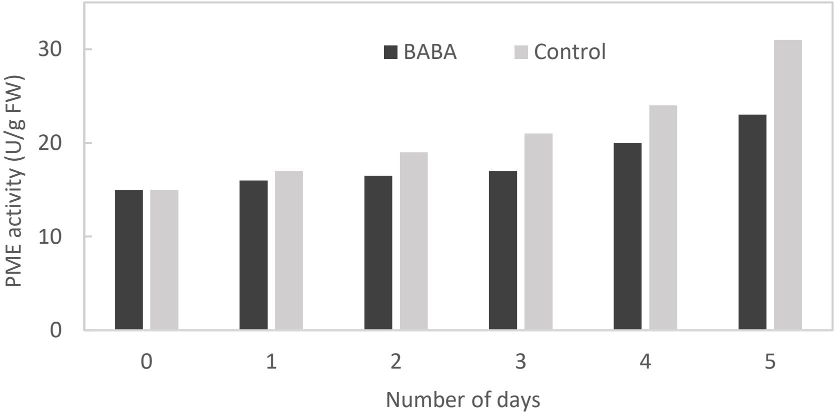

Fig. 8. Effect of BABA treatment on PME activity in sweet cherry fruit during storage at 20 °C. *Source:* [12].

Purification and Characterization of Glutathione S-Transferase from Cherry Laurel

Another enzyme found in cherry fruit is GST. It is a multifunctional enzyme that removes a high number of electrophilic xenobiotics in living organisms by binding to tripeptide glutathione (GSH) and plays important role in the detoxification system by various mechanisms. GST removes some toxic compounds from the system by covalent or non-covalent bonding and by incorporation into phase II reactions in the detoxification of xenobiotics. Furthermore, this enzyme produces antioxidant activity against the stress caused by organic hydroperoxides with peroxidase activity. GST is found in various organisms as in microbes, insects, fungi, fish, birds, mammals and plants [13].

GST was obtained from the cherry laurel flesh fruit. Two separate processes were used for enzyme purification: gel filtration and affinity chromatography. The sodium dodecyl sulphate electrophoresis method was used to determine enzyme purity. GST was analysed to obtain optimum pH, optimum temperature, optimum ionic strength, stable pH, and KM and Vmax values for glutathione and 1-chloro-2,4-dinitrobenzene. Furthermore, the inhibitory effects of metal ions and organic compounds were studied. It was found that Cd^{2+}, Ni^{2+}, Cu^{2+}, Mg^{2+}, and Ca^{2+} metal ions did inhibit activity of the enzyme, Ca^{2+} ions with the highest rate and Cd^{2+} with the lowest. Concerning organic molecules, ethylenediaminetetraacetic acid (EDTA), sodium dodecyl sulphate (SDS), benzoic acid, ascorbic acid, ethanol, and tocopherol (vitamin E) were used as the inhibitors and SDS was found to have the fastest inhibition rate and EDTA the slowest [13].

Activity of Softening Enzymes during Cherry Maturation

Important quality factor in cherries is the texture. During the mature the firmness of the fruit decreases due to structural changes in cell wall and middle lamella, which lead to cell separation and softening tissue. These changes occur due to the enzymes such as PG (Fig. 9), PME (Fig. 10), β-galactosidase (β -gal) (Fig. 11), cellulose and others. This study analyses activity of the four mentioned enzymes during the cherry maturation and storage in two cultivars [14].

Cellulase activity was not detected at any time during maturation or storage, but activity of PG, PME and β-gal was changing during maturation. The level of PG activity in cherries (0.32 units/g fresh weight) was relatively low compared to other fruits: avocado 0.8, peaches 4 to 6, pears 20 to 70 units/g fresh weight. PME activity was detected at earlier stages than PG activity and it was increasing continually during maturation and storage and reached a maximum at harvest in both cultivars. β-gal activity was also detected at the early stages of cherry ripening and the maximum was reached later in both cultivars than the peaks in either PG or PME [14].

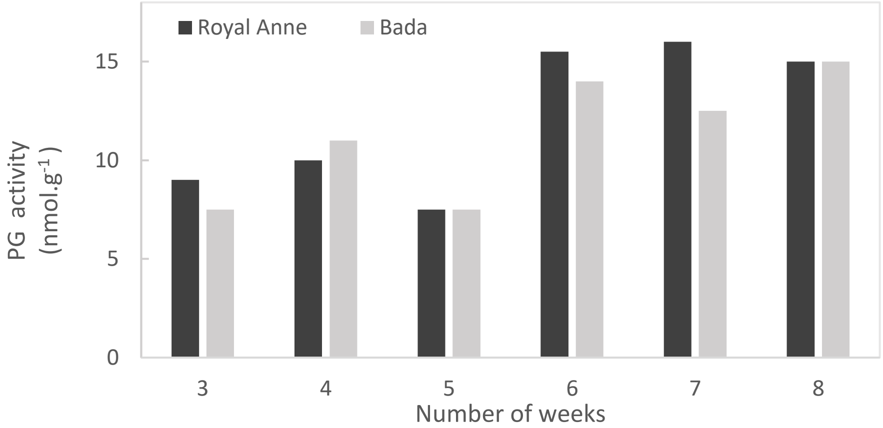

Fig. 9. Polygalacturonase activity in Bada and Royal Anne cherries. *Source: [14].*

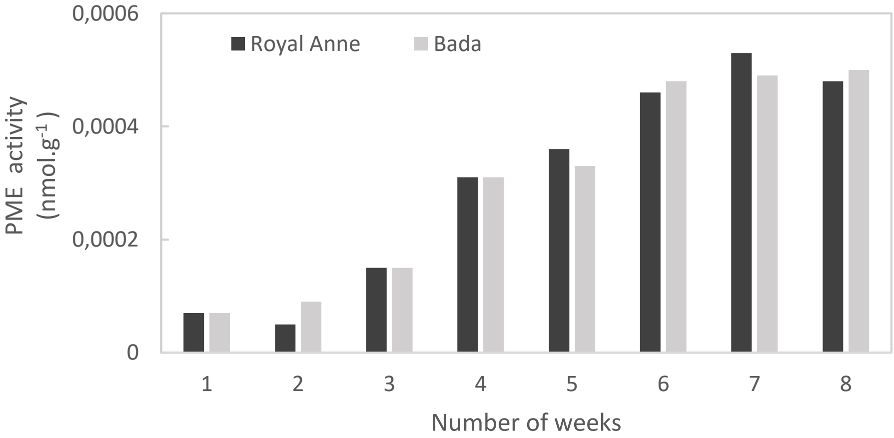

Fig. 10. Pectin methyl esterase activity in Bada and Royal cherries. *Source: [14].*

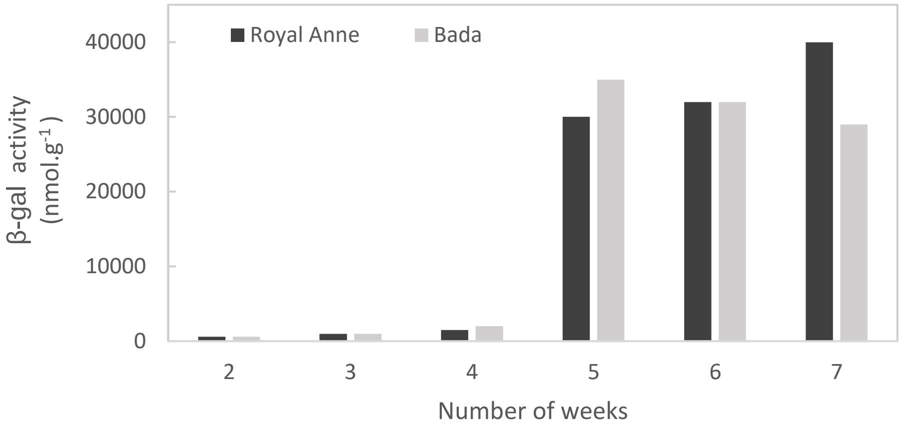

Fig. 11. β-galactosidase activity in Bada and Royal cherries. *Source: [14].*

Impact

As well as cherries, different kinds of fruit are also beneficial for human health because they contain vitamins, antioxidant compounds and fibre. During the harvest, preparation, and storage the fruit undergoes changes and loses both microbial and antioxidant properties. Following microbial contamination, oxidation is the second most significant cause of food deterioration inducing changes in flavour, odour, and nutritional value. The development of various methods and treatments for fruit preservation and extension of postharvest life of fruit is nowadays a high priority in the food industry [15].

This paper summarizes different methods used in treatment of cherry fruits developed in past years. The results showed that all mentioned treatments, particularly chitosan coating, BABA coating and storage in different atmospheres improved the postharvest life of cherry fruit. These findings are very interesting for possible real-life applications. The agricultural industry is and will benefit, first economically, able to maintain the freshness of the fruit and longer shelf-life and secondly, by introducing sustainable technology in food processing. Furthermore, the methods for isolation and purification of several enzymes found in cherries are discussed. This paper presents a review of studies published in past years concerning enzymes in cherries. Because we know that enzymes are important for the healthy functioning of the organism as well as on an industrial scale, we can expect the effects in different areas of human activity. With knowledge of the importance and content of enzymes in a particular type of fruit, an individual can plan an appropriate healthy diet. On the other hand, an impact on the development of the industry is expected, not only in the food industry but also in the production of fine chemicals.

Conclusion

Cherries are low caloric fruit with high content of important bioactive compounds and nutrients including fibre, polyphenols, carotenoids, various vitamins and minerals, and hormones. Nowadays, cherry fruit becomes more and more popular among consumers due to its health benefits. One of the main issues with production of cherries is their short shelf life as they darken and soften when stored. Several enzymes contribute to these changes and they have attracted attention of numerous researchers. Some experiments such as chitosan and MAP treatment successfully inhibited browning enzymes and slow down deterioration of the fruit. However, more studies should be carried out to find a way how to extend shelf life of this highly nutritious fruit even more and thus prevent its loss.

Conflict of interest

There are no conflicts to declare.

Acknowledgments

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IONIC LIQUIDS IN THE PRETREATMENT OF LIGNOCELLULOSIC BIOMASS

Héctor Rodríguez
CRETUS Institute, Department of Chemical Engineering, Universidade de Santiago de Compostela
E-15782, Santiago de Compostela, Spain; e-mail: hector.rodriguez@usc.es
https://orcid.org/0000-0002-6447-3590

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Abstract

The pretreatment is a key step in the processing of lignocellulosic biomass for its transformation into chemicals and materials of biorenewable origin. Ionic liquids, with their characteristic set of unique properties, have the potential to be the basis of novel pretreatment processes with higher effectiveness and improved sustainability as compared to the current state-of-the-art processes. In this opinion paper, the author provides a perspective on possible processing strategies for this pretreatment with ionic liquids, identifying different advantages as well as challenges to be overcome.

Keywords

Ionic liquid, biomass, lignocellulose, biorefinery, pretreatment, fractionation

Introduction

More than thirty years after the formal coinage of the term "sustainable development" [1], a tendency in the industry to shift to more sustainable processes is consolidated in the frame of the continuous improvement wheel. In 2015, the United Nations established a 2030 Agenda for Sustainable Development, including a set of sustainable development goals [2]. Although some of those goals are more specifically related to economic growth and industrial development, a strong interconnection exists among them, and their satisfactory achievement will be conditioned, for instance, by the further development of industrial processes leading to lower pollution and lower environmental impact. At present, however, a very relevant portion of plants and processes in the chemical industry and energy sector are still based on the utilization of fossil fuels or derived substances as feedstocks, with the subsequent generation of significant environmental issues and the non-sustainable depletion of natural resources. In the new context of sustainability and circular economy that impregnates the above-mentioned Agenda, there is a need for a decided switch to a new industrial platform to produce chemicals (including fuels) and materials, based on the utilization of renewable sources. The high volume of industrial production, which is expected to keep growing due to the gradual improvement of the life quality standards of our societies, poses a significant challenge on identifying the raw materials to feed such platform in a sustained fashion. An appealing candidate is lignocellulosic biomass, which is produced biorenewably by Nature at a sufficient pace as to cover the human demand of industrial production [3]. In addition, it exhibits other advantageous attributes: it presents a more homogeneous geodistribution than the fossil resources that sustain most of the global productive scheme nowadays; and, in contrast to other biorenewable sources, it avoids competition or direct interaction with the food market [4].

Although humankind has used lignocellulosic biomass in a variety of forms since prehistorical times, it was not until the identification of cellulose in the 19th century that its intrinsic chemical richness started to be unveiled. The three major components of lignocelluloses are the three biopolymers that mainly compose the complex non-uniform 3D structure of their cell walls: cellulose, hemicellulose, and lignin. Cellulose is a linear polysaccharide consisting solely of glucose monomers, with a strong network of intra- and intermolecular hydrogen bonds; hemicellulose is an amorphous, branched polymer involving C5 (xylose, arabinose) and C6 (glucose, mannose, galactose) sugar monomers (all of which can be highly substituted by acetyl groups); and lignin is a highly branched polymer biosynthesized from up to three aromatic monomers (coniferyl, sinapyl, and p-coumaryl alcohols) [3,5,6]. While the relative composition of cellulose, hemicellulose, and lignin in the cell wall of a plant is a function of the species, tissue, and maturity, lignocellulosic biomass can be generally claimed to contain 25-50 % cellulose, 15-35 % hemicellulose, and 10-35 % lignin [6]. The remaining fraction is made up of proteins, oils, and other organic and inorganic compounds, traditionally denoted as extractives and ashes. With all this

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chemical richness and versatility, it is clear that lignocellulosic biomass has great potential as the feedstock of reference for a biorenewable chemical platform for the industrial production of a wide portfolio of chemicals and materials. This is the basis of the concept of biorefinery [7]. However, the industrial exploitation of lignocellulosic biomass as a resource in the chemical sector has focused historically on just one of the biopolymers, namely cellulose; thus, neglecting the potential of hemicellulose and lignin to contribute to the biorefinery paradigm. It is widely accepted at present that the development of viable biorefinery schemes should consider an integral valorization of the three biopolymers [4,8,9]. Thus, alternative technologies are needed for a better valorization not just of cellulose but also of hemicellulose and lignin.

The efficient exploitation of lignocellulosic biomass is typically hampered by its recalcitrant character, which can be seen as the result of a natural evolution to resist degradation. This recalcitrance makes difficult the access or the disengagement of the constituent biopolymers for their suitable transformation in subsequent process stages. The recalcitrance of lignocelluloses stems mainly from the crystallinity of cellulose, the hydrophobicity of lignin, and the encapsulation of cellulose by a lignin-hemicellulose matrix [10]. To benefit from all the chemistry naturally embedded in its constituent biopolymers, the accessibility to these compounds within the lignocellulosic matrix must be improved. To assist in this accessibility improvement, the lignocellulosic feedstock is typically subjected to a pretreatment step. This is often a key step that pursues modification of the lignocellulosic structure and alteration of the pore size [11,12]. A variety of pretreatment methods have been developed for the processing of lignocellulosic biomass [6,13,14]: mechanical comminution, dilute acid hydrolysis, alkaline hydrolysis, steam explosion, ammonia fiber explosion, organosolv pretreatment, biological pretreatment... Despite this variety, the developed pretreatment methods present a number of drawbacks and are still far from leading to a satisfactory performance, with poorly sustainable conditions being typically involved (resulting in operational difficulties and important pollution emissions [15], as well as undesired degradation of the biopolymers), and accounting for a relevant cost within the overall processing chain [14]. There is therefore a clear need for the development of better pretreatment methods.

Ionic liquids – Can they help?

In the development of a sustainable biorefinery, the chemical products used or generated should be as environmentally friendly as possible, avoiding harmful substances. Additionally, the processes to be developed within this paradigm should maximize the transformation of the renewable raw materials into the desired final products [16,17]. In this line, with their unique characteristics and a versatile capacity for the dissolution of lignocelluloses, ionic liquids have the potential to offer attractive alternatives as auxiliary substances within the lignocellulosic biorefinery endeavor, as commented below. Ionic liquids are salts with a relatively low melting or glass transition temperature (usually a mark of 100 °C is considered) [18]. Due to their ionic nature, ionic liquids have a negligible vapor pressure under usual operation conditions of most industrial processes. Thus, as opposed to conventional molecular solvents, their use would generally avoid solvent losses by evaporation (with the subsequent atmospheric pollution) and the generation of flammable atmospheres in the process plant. Although it is difficult to generalize other properties for the entire family of salts that meet the ionic liquid definition, many of them also exhibit a wide liquid range, with the upper limit determined by an acceptably good thermal stability, and a great solvation ability for a broad range of compounds. These unique characteristics have led to a prolific academic research on ionic liquids since the late 1990s, and to a great interest from the industry, resulting so far in a number of applications in diverse fields that have already reached pilot plant or full commercialization status [19].

One of the areas in which ionic liquids are showing great promise is in the processing of lignocellulosic biomass. The seminal work in this area, dating from 2002, reported the discovery of the capacity of some ionic liquids to dissolve cellulose without derivatization, in high concentrations and at relatively mild conditions [20]. In the following years, reports also appeared on the dissolution of lignin and partial or total dissolution of diverse lignocellulosic materials, including woody biomass, in ionic liquids under similarly mild conditions. Since then, the number of researchers attracted by the intersection of lignocelluloses and ionic liquids has kept growing, as well as the knowledge of the science behind the observed dissolution capacities. Broadly, ionic liquids that can dissolve cellulose are also capable of dissolving lignocelluloses; whereas there are other ionic liquids that are able to dissolve lignin but not cellulose [21–23].Hemicellulose is, in general, more easily dissolved in conventional solvents than either cellulose or lignin, and thus no emphasis has been put on finding ionic liquids that can selectively dissolve hemicellulose [23].

This versatility of ionic liquids in dissolving numerous lignocellulosic materials, as well as their individual constitutive biopolymers in different extents, enables the envisioning of diverse strategies of pretreatment for the fractionation of these biopolymers and their subsequent exploitation within biorefinery schemes, as discussed in the next sections. Thanks to the mildness of the conditions and some of the inherent characteristics of ionic liquids, these novel approaches have great potential to lead to advantageous performances with respect to conventional methods.

Dissolution-based strategies for the fractionation of lignocellulosic biomass with ionic liquids

Some ionic liquids have proven their capacity to dissolve completely lignocellulosic materials, including woody biomass [5,24], under certain conditions. In such capacity, the chemical structures of both the cation and the anion constituting the ionic liquid are relevant. Whereas there is a good consensus about the need of the anion to have a high hydrogen bond basicity [5,6] (anions such as acetate, chloride, hydrogensulfate...), the required structural features for the cation remain more unclear (even though it is evident that, for a given anion, some of them work and some do not). Additionally, operating parameters such as temperature, biomass nature, particle size, solute-to-solvent load, etc. have a strong influence in this dissolution capacity [6,25]. In any case, these lignocellulose-dissolving ionic liquids enable an approach consisting of the integral dissolution of the biomass, followed by stages for the fractionation of the dissolved biopolymeric fractions, looking for the (total or partial) separation of the constitutive biopolymers. This approach is illustrated in Fig. 1. Due to the non-volatile character of both the ionic liquids and the solutes dissolved, the regeneration of the lignocellulosic fractions from the ionic liquid is not viable through unit operations based on vaporization of compounds. Liquid-liquid extraction with an organic solvent could be in principle an option, but the difficulty of finding such extraction solvent with greater preference for the dissolved fractions than the biomass-dissolving ionic liquid discourages this option. A more plausible strategy is the regeneration of the biopolymeric fractions by addition of (molecular) solvents miscible with the ionic liquid and acting as antisolvents for the dissolved material, thus precipitating it out of the solution [5,25,26]. The design of an adequate precipitation scheme with the appropriate set of antisolvents will lead to a total or partial fractionation of the biopolymers [24,25,27], depending on the ability of the ionic liquid to actually disengage the different biopolymers in the lignocellulosic matrix upon dissolution. In Fig. 1, one such generic precipitation scheme is presented. After removal of the biopolymeric precipitates via a unit operation for solid-liquid separation (e.g., filtration), the antisolvent has to be separated from its mixture with the ionic liquid, for recycling of all components in the process. For this separation, operation units based on the creation of a vapor phase (e.g., flash distillation or evaporation) will be normally considered. Consequently, antisolvents of intermediate volatility will be desirable, thus balancing two aspects: the energy required for their removal by vaporization from the mixture with the non-volatile ionic liquid for recycling of these substances to the process; and the safety and environmental risks associated with a too volatile compound. Additionally, the proposed antisolvent should exhibit acceptably good green credentials so that the general sustainable character of the proposed process would not be compromised.

While the structures of lignin and hemicellulose remain essentially unaltered after treatment with the approach described in Fig. 1 [28], the crystallinity of cellulose in the regenerated lignocellulosic biomass fractions is lower than in the untreated material. The crystalline structure of cellulose changes from the recalcitrant native structure ‘Cellulose I’ to the structure ‘Cellulose II’ with improved processability, and there is a loss in fibrillar ordering that results in a higher amorphous component [5]. This is an aspect of great interest for a better utilization of the obtained cellulose as a precursor of e.g., derived polymers or biofuels, since the amorphous cellulose will be more accessible to chemical and enzymatic methods for its transformation.

A second approach, as an alternative to the solubilization of the entire lignocellulosic material, is based on the chemical disruption of the lignocellulose ‘composite’ without achieving total dissolution in the ionic liquid [5]. For example, a selective (partial) extraction of lignin from the lignocellulosic matrix can be performed with some ionic liquids able to dissolve lignin but not cellulose [5,23]. An integral scheme based on this approach is shown in Fig. 2. Since cellulose will not undergo actual dissolution, its recalcitrant crystalline character will be essentially preserved (as in most common pretreatment methods to date), as opposed to what has been commented in the paragraph above. Therefore, this approach may be more attractive in those cases in which preservation of the crystallinity is of interest and cellulose constitutes one of the final products of the biorefinery. Additionally, the set of ionic liquids that can be used in this approach is less restricted than the set of ionic liquids with the capacity to integrally dissolve lignocellulosic materials [21], providing a greater degree of flexibility in the ionic liquid selection. For example, ionic liquids comprising sulfonate- or sulfate-based anions may be considered (although care must be taken with ionic liquids generating less basic or even acidic environments, as a greater conversion of hemicellulose to humins and other degradation products may occur) [5]. Nevertheless, the use of molecular solvents is also necessary for the regeneration of the dissolved biopolymer fractions from the ionic liquid solution in this alternative approach.

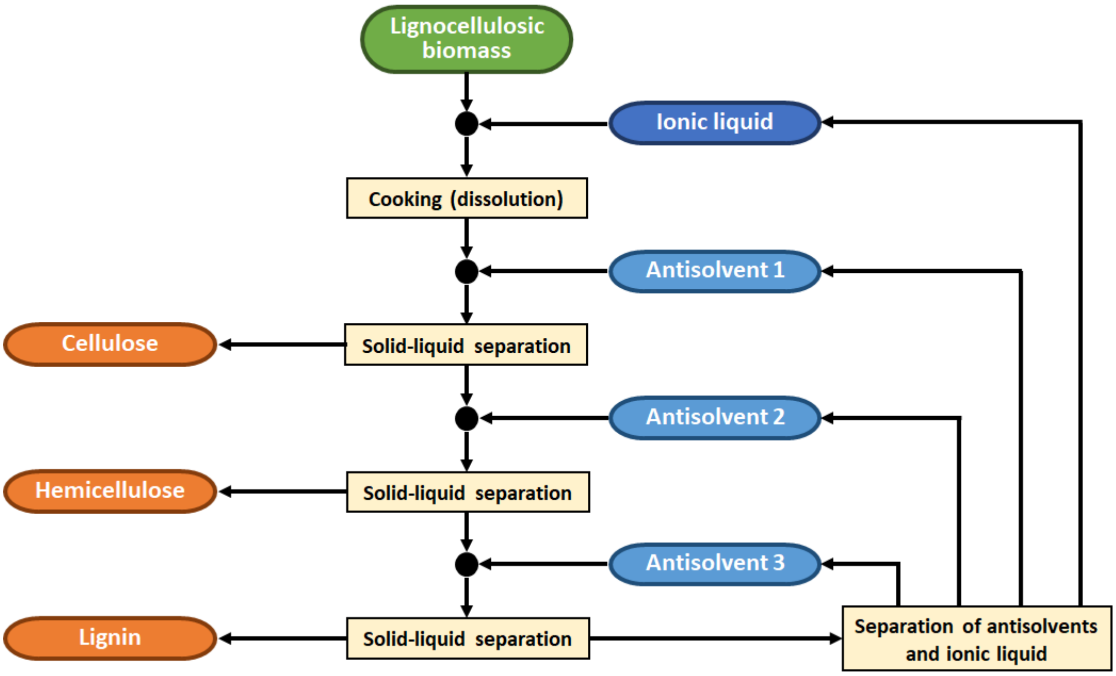

Fig. 1. Idealized scheme of the integral dissolution approach for the fractionation of lignocellulosic biomass, considering one of the many possible strategies for selective precipitation of the dissolved biopolymer fractions by addition of antisolvents.

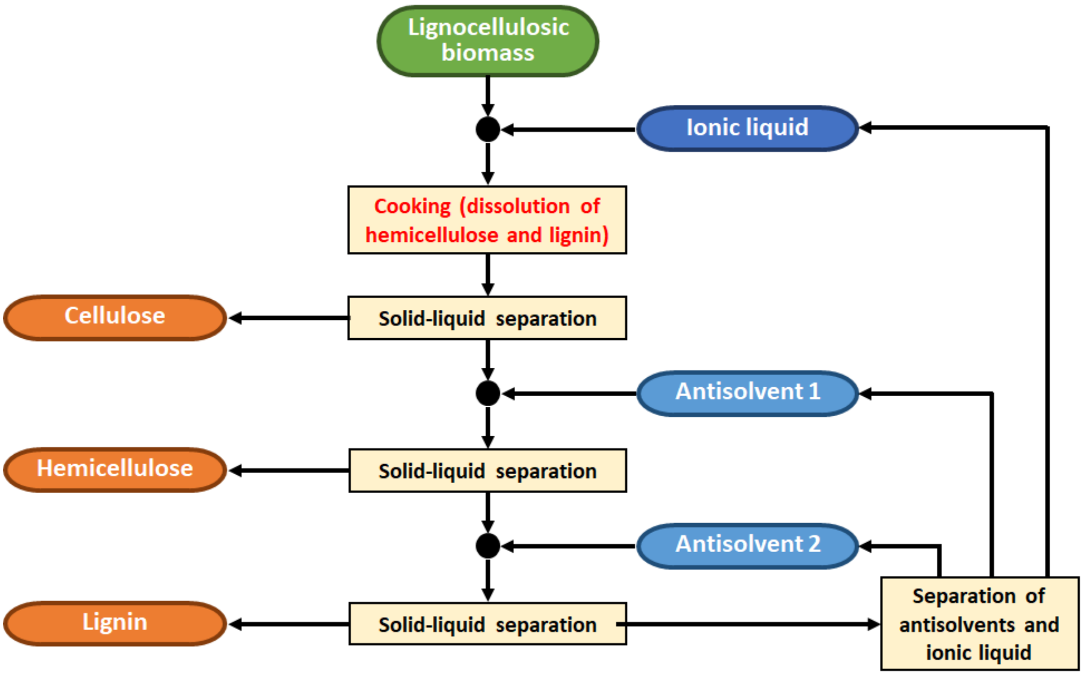

Fig. 2. Idealized scheme of a strategy based on the partial dissolution approach for the fractionation of lignocellulosic biomass. In this case, simultaneous extraction of hemicellulose and lignin from the lignocellulosic matrix is considered, although alternative strategies are possible.

Besides the use of neat ionic liquids for the total or partial dissolution of the lignocellulosic materials, in either of the approaches the utilization of solvent systems combining ionic liquids with molecular solvents (e.g. water, acetone, aprotic polar solvents such as dimethylsulfoxide, etc.) has also been tested for a variety of biorefinery targets [22,23]. These combinations, except in the case of water, can be considered to lie within what is termed 'organic electrolyte solutions'. These solutions may offer some advantages, such as the lowering of the viscosity of the dissolution medium (which is one of the major drawbacks when using pure ionic liquids – see next section), or the possibility of utilizing ionic liquids or organic salts with a too high melting temperature as to be used in neat. On the other hand, the presence of the molecular cosolvent will imply the complications already commented for the antisolvents. Moreover, it must be considered that the special dissolution capacity of ionic liquids will be a sensitive function of the concentration, and the equilibrium between this dissolution capacity and a suitable set of fluid attributes for the organic electrolyte solution will be delicate.

Process-related problems and some potential ways of overcoming them

For ionic liquids to actually contribute to the fulfilment of the biorefinery paradigm through any of the process variants investigated, there are still important challenges to be addressed [5,14,22,29]. A first group refers to the nature of the ionic liquids themselves and will be discussed in a separate section. The second group includes challenges connected with different aspects of the processing. For example, the efficient recycling of the ionic liquid has been identified, by means of technoeconomic analyses, as one of the most critical aspects [30–32], even with projected ionic liquid costs corresponding to their scaled-up production. One of the necessary goals to succeed in this regard is the effective removal of any remaining biomass fractions from the ionic liquid after the antisolvents addition, to avoid the build-up of unwanted pretreatment byproducts that can decrease performance [14,33]. The cellulose-rich fractions will probably not pose a major problem, as they will be precipitated out of the solution in a reasonably easy manner; at least if an adequate engineering approach is adopted (for example, addition of the antisolvent under gentle stirring conditions) so that potential problems of gelation are avoided. However, the precipitation of hemicellulose and lignin may be more complicated, as these biopolymers have a greater tendency to non-negligible solubilities in the mixtures of ionic liquids and antisolvents. Although the fate of hemicellulose in the precipitation step of ionic liquid based pretreatments has received less attention than that of cellulose and lignin in the literature to date, it is clear at least for lignin that total precipitation (including small polymeric fragments) is likely to require excessively large amounts of antisolvent [34,35]. Subsequently, the recycling of the ionic liquid by vaporization of those amounts of antisolvent would require a prohibiting energy input. Two possible alternatives to overcome this issue are schematized in Fig. 3. A first alternative would be to remove those hard-to-precipitate fragments of biopolymer by liquid-liquid extraction with a suitable solvent (immiscible with the ionic liquid) [36]. This strategy will only make sense if a solvent is found with the capacity for effectively extracting the biopolymeric fractions from the ionic liquid medium at low solvent-to-ionic liquid ratios, as the regeneration of those fractions would be eventually done by vaporization of the extracting solvent. A second alternative may consist of the in-situ transformation (depolymerization) of the biopolymer fractions in the ionic liquid medium [34], and then recovering the generated (volatile?) products either by solvent extraction or by a vaporization technique (the latter is illustrated in Fig. 3).

The scheme proposed in Figure 3b represents a step towards process intensification. Depending on the profile of the final products that constitute the target of the specific biorefinery effort, process intensification can be pushed well further, resulting in the reduction or avoidance of antisolvents and energy involved in the precipitation scheme of the biopolymer fractions from the initial pretreatment step. An example of process intensification is the one-pot integration of the stages of pretreatment, saccharification and fermentation for the production of biofuels [31,32]. In this case, the use of ionic liquids showing compatibility with the biocatalyst(s) used for the saccharification and fermentation will be a requirement.

Besides avoiding the build-up of biomass-derived substances in the ionic liquid, another key aspect for its efficient recycling (and for the economy of the entire process) is the energy required for its separation from the antisolvents after recovery of the biopolymer fractions. Obviously, this will be a function of the amount of antisolvent needed to cause the precipitation of the solutes. However, little emphasis has been put in the literature on the quantification of the minimum antisolvent to be added [26], despite its critical role in the conception and design of a process to be scaled up for application at an industrial level. As the proposed pretreatments progress towards commercialization, a focus on this quantification is gaining relevance [34,35].

The nature of the antisolvents is also relevant: in addition to the adequate balance in volatility that was already commented in the previous section, they should preferably have low/moderate specific heat and heat of vaporization, thus reducing the required energy input during the vaporization stage for the recycling. The latter is probably the Achilles heel of the use of water as antisolvent. To date, water has been the most common choice for this role in the literature, and indeed its 'intrinsic' green credentials are unbeatable. However, its high specific and vaporization heats, and a relatively high boiling temperature, imply a presumably excessive energy penalty for its elimination by vaporization at the stage of recovering the ionic liquid.

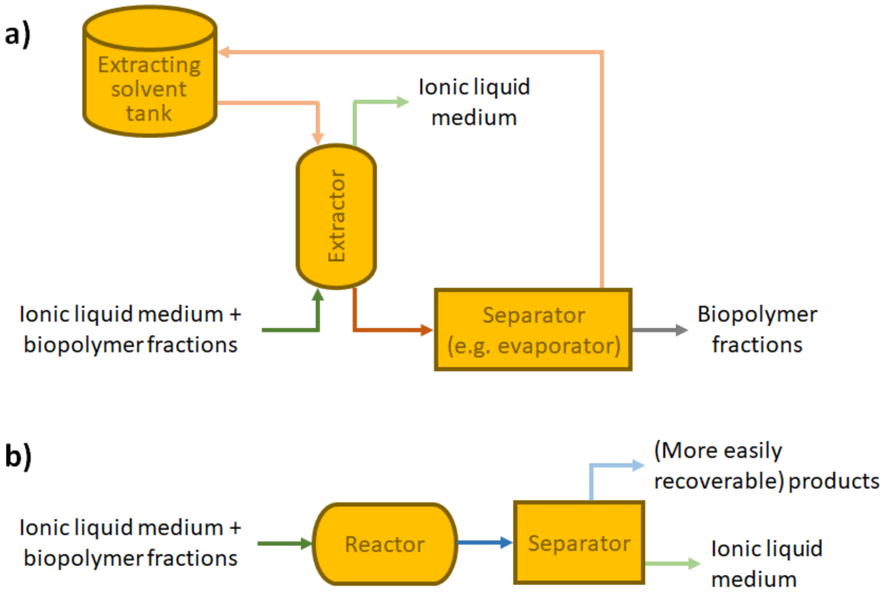

Fig. 3. Alternatives to the antisolvent strategy for the recovery of hard-to-precipitate biopolymer fractions from the ionic liquid medium: a) liquid-liquid extraction with an extracting solvent; b) in-situ transformation of the biopolymer(s) in the ionic liquid medium, with subsequent removal of the generated products.

Alternatives to the use of water or conventional organic solvents in their role as antisolvents may be of interest. The extraction with supercritical fluids, particularly CO_2, was considered in general for the recovery of non-volatile solutes from ionic liquid solutions [37], and it could be potentially interesting for the extraction of the soluble biopolymeric fractions resulting from the pretreatment of lignocellulose feedstocks. However, this technology implies high investment and operation costs, and it may render the biorefinery effort non-viable from an economic perspective. A second possibility using CO_2 as antisolvent, at lower pressures, can be of application in the case of ionic liquids that react with this gas to yield a solid, as it is the case for example of the archetypal biomass-dissolving ionic liquid 1-ethyl-3-methylimidazolium acetate [38]. The economically viable reconstitution of the neat ionic liquid is still in question, and more work is required for further development of this approach.

Viscosity is another issue that can impose important limitations in processes based on ionic liquids for the pretreatment of lignocellulosic materials. Although ionic liquids often exhibit an appealing set of properties for their use as solvents in potentially sustainable processes [18,39], one of their most recurrent drawbacks is their relatively high viscosity, as compared to conventional molecular solvents. This viscosity is additionally increased upon the dissolution of (ligno)cellulosic solutes, generating relevant kinetic restrictions in the process [40]. The use of a molecular solvent as cosolvent of the ionic liquid in this kind of processes, assuming that it does not reduce significantly the dissolution capacity of the ionic liquid, would facilitate the mass transfer phenomena in the process as a result of the diminution of the viscosity [39]. Such viscosity decrease of the fluid medium would also be beneficial for the process from an engineering perspective. Moreover, the use of a cosolvent together with the ionic liquid may be a tool for the modulated control, by variation of the relative composition of ionic liquid and cosolvent, of the solubility capacity of the resulting solvent fluid, with potential application in the fractionated precipitation of the dissolved biopolymeric fractions [34,41]. This is illustrated in Fig. 4, where it can be observed that the cosolvent becomes the antisolvent as its concentration in the fluid medium is increased. This strategy would yield in parallel the benefit of simplifying the process in the sense that it would reduce the number of auxiliary substances involved in the process, thanks to the adoption of one single substance as cosolvent and as fractionation antisolvent. An extra point in the utilization of this single cosolvent/antisolvent would be that the requirement of elimination of antisolvent from its mixture with the ionic liquid would be only partial, avoiding a very important percentage of the energy that would be actually required to regenerate the ionic liquid in a pure condition [42].

The implementation of improvements in the efforts to address the above-mentioned problems will help to make the pretreatment with ionic liquids viable at an industrial scale. Nevertheless, the core problem to achieve an appropriate valorization of the lignocellulosic feedstock in an integral manner with the proposed technology lies in the development of ionic liquid-based fluids capable of a cleaner fractionation of the constitutive biopolymers. The schemes in Figures 1-4 have assumed perfect separation of all three major biopolymers, but the current results have not reached that point. Moreover, the particle sizes that have been explored in most of the research to date are clearly smaller than the common particle sizes in current pretreatment processes with other technologies. If the ionic liquid technology is able to get a clean fractionation, maybe a smaller particle size than the one used in other technologies can be accepted. However, this has to be sufficiently balanced as to avoid an excessive cost of the reduction of the particle size of the biomass feedstock, which would render the entire process non-viable from an economic point of view.

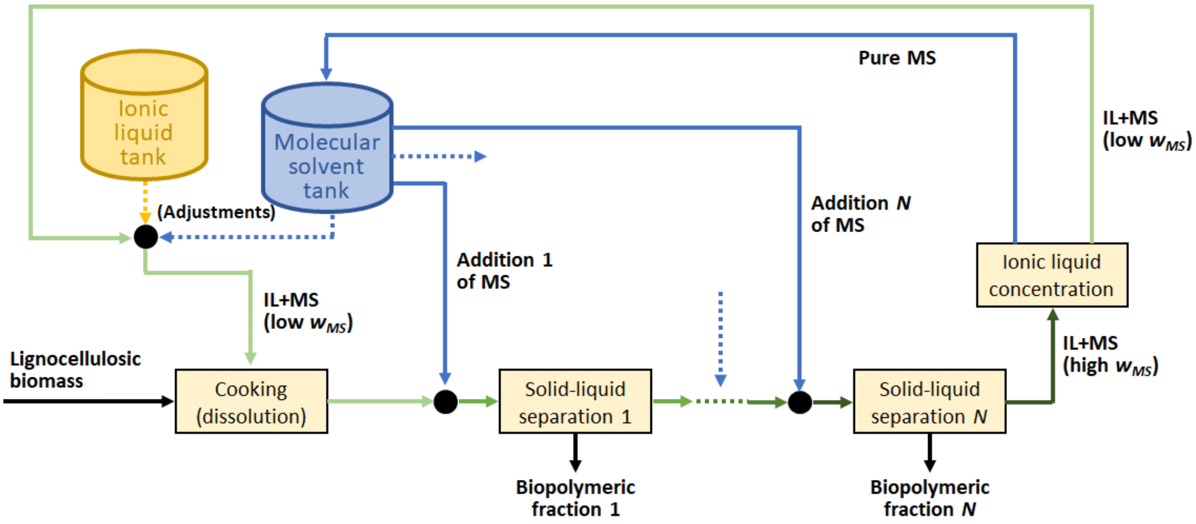

Fig. 4. Proposed use of a single substance as a cosolvent of the ionic liquid in the pretreatment step (for lowering of the viscosity) and as an antisolvent for fractionation of the dissolved biopolymeric fractions. (Legend: IL, ionic liquid; MS, molecular solvent; w_{MS}, mass fraction of molecular solvent in the IL+MS mixture.)

Expanding the processing options: a non-dissolution approach

The research efforts made so far on the pretreatment of lignocellulosic biomass with ionic liquids have been based mostly on the partial or total dissolution of the biomass in the ionic liquid. Due to the non-volatile nature of both the ionic liquid and the biopolymeric constituents of the biomass, this implies the use of antisolvents and problems of efficient recycling of the ionic liquid, as already commented. To avoid these problems, an alternative pretreatment scheme based on non-dissolving conditions may be envisioned (Fig. 5), depending on the objectives of the specific biorefinery context. Some ionic liquids show no capacity to dissolve (ligno)cellulosic materials but are however capable of interacting with them in the solid phase (without carrying out dissolution). The result of such interaction may be for example a reduction in crystallinity of the cellulose fraction, which will facilitate the reaction and transformation of this biopolymer in subsequent stages [43,44]. After that, the other biopolymers originally composing the lignocellulosic matrix will be likely more accessible. Importantly, due to the non-dissolving character of this approach, the use of antisolvents to precipitate dissolved fractions is not necessary in principle, and the separation of the pretreated biomass and the ionic liquid can be achieved by simple filtration. (Losses of ionic liquid impregnating the filtered solid, that will have to be washed out, can be anticipated though.)

The choice of ionic liquid for the non-dissolving pretreatment of Fig. 5 does not necessarily exclude those ionic liquids known to have the capacity to dissolve lignocellulosic materials. Such dissolution capacity may be hampered at certain conditions, for example at low temperature (which would be interesting from the perspective of reduction of energy consumption during the pretreatment step, while also reducing the risk of undesired thermal degradation of substances in the system). Alternatively, this dissolution capacity might be also neutralized by addition of a cosolvent, while keeping the ability of the resulting fluid system to generate a sufficient interaction with the lignocellulosic matrix as to lead to an effective pretreatment in accordance with the scheme of Fig. 5.

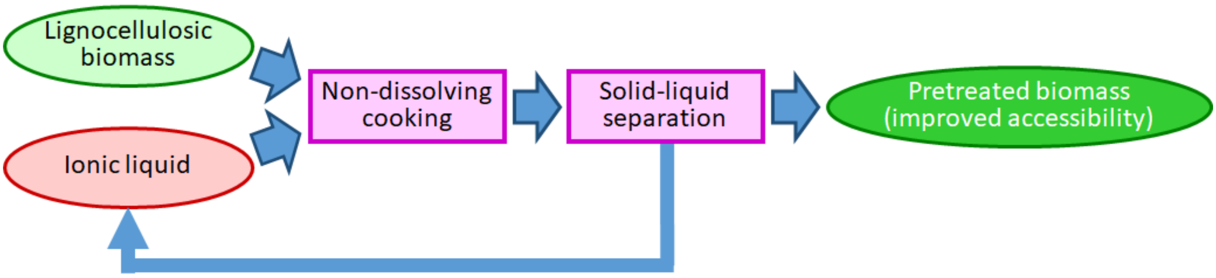

Fig. 5. Non-dissolving approach for the pretreatment of lignocellulosic biomass with ionic liquid.

A focus on the general characteristics of ionic liquids themselves

In parallel to the search of ionic liquids with better pretreatment performance in terms of dissolution, deconstruction, fractionation or related target, attention has to be paid to the intrinsic characteristics of those ionic liquids. Aspects such as cost, toxicity, biodegradability, or issues on thermal and chemical stability in the long term are matters of particular concern.

Ionic liquids are, in general, the most expensive solvents currently explored for the dissolution of lignocellulosic biomass [5,6]. Although the current commercial prices will not be representative due to the limited size of their mostly research-oriented production, the price of ionic liquids produced on a large scale will be conditioned largely by the cost of the cation and anion price [45]. With this in mind, ionic liquids with estimated costs as low as ca. $1/kg have been produced by protonation of cheap organic amines with standard organic or mineral acids, and applied successfully to the pretreatment of lignocelluloses [32,46]. Our experience with protic ionic liquids, nonetheless, invites to think of the existence of a non-negligible equilibrium between the ionized and neutral forms in the presence of some water (which can easily accompany the biomass up to a certain percentage). Thus, further research shedding some specific light on this aspect for those ionic liquids would be welcome, to guarantee that problems associated with strong acids and bases in some conventional pretreatment methods do not arise in here, too. Combined with the same cheap anions (e.g., chloride, acetate), some popular families of permanent cations such as tetraalkylammoniums or tetraalkylphosphoniums may lead to aprotic ionic liquids with affordable cost for industrial application as well. All in all, 'sufficiently low price' only acquires a meaning in the context of a given performance in the frame of an overall process; and it will be the corresponding economic viability study of the entire process what will dictate whether the cost of the ionic liquid is acceptable or not.

Ideally, the ionic liquids of choice should exhibit low or negligible toxicity and full biodegradability, potentially imposing a significant challenge when combining it with the list of other desired characteristics, and without compromising high performance for the intended application of pretreatment of lignocelluloses. Toxicity and biodegradability in the family of ionic liquids are tremendously diverse, and although some connection of these parameters with structural features of the ionic liquids have been identified, a full understanding remains elusive [47,48]. Nevertheless, it is generally acknowledged that the use of molecules from bio-renewable sources as anionic and/or cationic precursors is one of the most promising strategies to generate biocompatible ionic liquids [49]. Amino acids, non-nutritive sweeteners, glucose, carboxylic acids... could be the raw materials of choice in the ideal manufacturing of (both the cation and the anion of) bio-based ionic liquids [49]. In this line, and for the pretreatment of lignocellulosic biomass, an interesting effort has been made by developing ionic liquids with constitutive ions originating from the biomass itself [50]. Unfortunately, the associated synthetic steps involved materials and procedures with low sustainability character. The concept, though, remains certainly valid, and further research in that direction might lead to appealing results. In any case, the biocompatibility of the pretreatment fluid will be critical in those cases of process intensification where the pretreatment stage is combined with biocatalyzed stages such as saccharification or fermentation [32].

Chemical and thermal stability are also relevant in the selection of an ionic liquid for its utilization in a process for the pretreatment of lignocellulosic biomass. Within those ionic liquids typically investigated for such application, a paradigmatic source of undesired chemical reactivity with lignocellulosic biopolymers is represented by the acidic proton at the C2 position of 1,3-dialkylimidazolium cations paired with sufficiently basic anions [51,52]. A possible option to keep utilizing this kind of ionic liquids while avoiding the undesired reaction might be the pretreatment at lower temperatures, where the corresponding kinetics will not be favored. This will be obviously at the risk of rendering the biomass pretreatment less effective, or even ineffective. The suggested reduction of the processing temperature may be also motivated by a thermal degradation issue. Although the onset decomposition temperature from a dynamic run in a thermogravimetric analysis constitutes an overestimation of the real maximum temperature at which the ionic liquid can be operated, it is still taken frequently as the reference for evaluating the temperature limit of usage of the ionic liquid. For short pretreatment times, a more conservative evaluation of the onset decomposition temperature from the same dynamic thermogram (for example calculating such onset for a small decomposition percentage of the ionic liquid sample) might be fine [41]. However, and particularly for longer pretreatment stages at elevated temperature, a safer estimation of the maximum operation temperature will be obtained from isothermal thermogravimetric analyses. The latter are still barely reported in the literature, despite their capital importance in guaranteeing the thermal stability of the ionic liquid in the mid/long-term. Studies of this kind, available for some ionic liquids proposed for the pretreatment of (ligno)cellulosic materials, reveal relevant reductions in the estimated maximum operation temperature if compared to the regular onset temperature obtained by dynamic thermogravimetric analysis [43,53].

One further characteristic to take into account could be the corrosive character of ionic liquids. In this regard, the scientific literature has focused mainly on the anti-corrosion properties offered by some ionic liquids, which do not correspond with those typically proposed for the pretreatment of biomass. For the latter, there is an enormous lack (and need) of information.

High viscosity can be also considered as an inherent characteristic of many ionic liquids. This issue, however, has already been discussed in a previous section.

Moving forward...

Ionic liquids offer a basis for a greatly versatile technological platform for the pretreatment of lignocellulosic biomass, in a frame of potentially improved sustainability. Promising results have been achieved over the last decade and a half. In the route towards successful industrial implementation, the search of ionic liquids with better performance must continue. In the progress to higher technology readiness levels, the following aspects should be considered:

- Improved tolerance to water in the system, as the performance of most ionic liquids explored to date decreases sharply in the presence of water.
- Satisfactory pretreatment using bigger particle sizes, so that the large energy consumption in the preparation of the feedstock for the process can be reduced [5]. A movement from sawdust to industrial chip size, or close, has to be made.
- Demonstrable flexibility to deal with the common variability in the characteristics of the supplies of a given lignocellulosic source. Ideally, this flexibility should be extended to the possibility of working with different types of lignocellulosic species (feedstock-agnostic processes).
- Fine control of the quantity of antisolvent(s) to be used, in dissolution-based approaches, for the precipitation of the (ligno)cellulosic fractions in the engineered context. This will be critical to minimize the energy penalty associated with the subsequent separation of antisolvent and ionic liquid for their recycling to the process [26].
- Choice of stable ionic liquids as biocompatible and as cheap as possible, and preferably derived from renewable raw materials [17].

The ionic liquid does not have to be necessarily at the core of the solution. The above-mentioned versatility of the ionic liquid technology enables its combination with the conventional pretreatment methods already in place [29], as well as with other alternatives under investigation (e.g. microwaves, autohydrolysis...). The use of the ionic liquid as additive in some of these scenarios, or as the main actor of just a specific step inserted in a general process, remains quite largely unexplored. This type of use of the ionic liquid would likely introduce a greater flexibility in terms of the cost requirements of the ionic liquid.

Most works to date on the pretreatment of lignocelluloses with ionic liquids have focused on what could be called ‘simple’ ionic liquids, constituted by one type of cation and one type of anion. This is the simplest and best approach to connect the observed pretreatment performances with specific ions or cation-anion pairs. Once these connections are acceptably identified, nothing prevents us from formulating a multi-ion solvent, for example by combination of ‘simple’ ionic liquids (or even higher-melting salts that do not qualify strictly as ionic liquids), allowing an optimization of the pretreatment performance and/or the properties of the pretreatment fluid. For instance, eutectic mixtures can be generated by such combination of ‘simple’ ionic liquids, integrally preserving the ionic liquid nature of the resulting fluid and enabling its utilization to pretreat biomass at a lower temperature than what would be possible for the ‘parent’ ionic liquids [54]. Statistical mixtures of ionic liquids are another example of multi-ion fluids, where several similar ions (e.g. dialkylimidazolium cations with alkyl substituents of different lengths) are produced in fixed molar ratios resulting from the statistical combination of the starting materials in a one-pot reactive step [55]. Most probably, the statistical mixture will perform very similarly to the ‘single’ ionic liquid in which it is based, with the advantage of potentially having a much lower cost of production. The existence of such one-pot synthetic procedures for the preparation, for instance, of statistical mixtures of some imidazolium-based ionic liquids from cheap starting materials may provide better opportunities for the application of these a priori too expensive ionic liquids in scaled-up processes [55].

As it was previously mentioned in this article, the combination of the ionic liquid with a molecular (co)solvent is another possibility of interest. The idea is to have a cosolvent that can strongly reduce the viscosity (thus facilitating the mass transfer processes) while not negatively affecting the pretreatment capacity in a substantial manner. It is true that, inevitably, the participation of the molecular cosolvent will imply some volatility and associated drawbacks for the pretreatment fluid. Due to the peculiarities of interaction of the ionic liquid with the lignocellulosic biomass, together with its ionic character, the best candidates among the portfolio of molecular solvents seem to be the polar aprotic solvents. Unfortunately, the solvents currently available in this category score quite badly in terms of sustainability [56], perhaps with the only exception of dimethylsulfoxide and somehow acetonitrile. Therefore, at present, it may be difficult to come up with a combination of ionic liquid and molecular solvent that be effective for the pretreatment while presenting acceptably good green credentials. Advances in the development of alternative protic apolar solvents to the classical ones, which is a general need in the chemical fields, would open new avenues for this strategy of a hybrid ionic-molecular solvent for biomass pretreatment. In any case, it must be noted that the introduction of volatile organic cosolvents or antisolvents will counteract some of the typically claimed benefits of the use of ionic liquids in processes, such as the lack of contribution to the air pollution or the non-generation of atmospheres that pose a health and safety risk in the work area. The solubility properties are clearly critical in the selection of these cosolvents/antisolvents involved in the precipitation scheme, but this selection should be also guided by a holistic consideration of their properties in the context of the process.

Other potential approaches of interest that can be pursued have already been commented in different sections of this article. One example is the possibility of having the same substance acting as a cosolvent and as antisolvent, depending on its concentration; or at least minimizing the number of working substances in the dissolution and precipitation scheme of the pretreatment process. Another example relates to process intensification, with the integration of the pretreatment stage with subsequent stages (especially if the biorefinery process is oriented towards a particular type of product, such as biofuels), through the utilization of ionic liquids with good biocompatibility.

Finally, it is worth mentioning that research on ionic liquids for the pretreatment of lignocelluloses may provide knowledge that can be beneficial for the envisioning of alternative pretreatment methods based on related solvents (e.g. imidazole [57]) or fluid mixtures (e.g. eutectic solvents resulting from mixtures involving a salt, or a hydrogen-bond donor and a hydrogen-bond acceptor [58,59]).

All in all, ionic liquids with their unique properties constitute a very attractive family of substances for biomass processing in a biorefinery context. However, there is a need to overcome key challenges for the development and implementation of commercially viable processes, in which the global process economy together with environmental and social impacts have to be properly optimized [29]. Further research efforts and intensive collaboration of industry and academia will be critical to help progressing in the scale of technology readiness levels and consolidate lignocellulosic biomass pretreatment processes based on this technology as an industrial reality of great benefit for a Society that must become necessarily more sustainable.

Impact

Ionic liquids, with their unique attributes, have the potential to be the basis of novel processes for the pretreatment of lignocellulosic biomass with improved sustainability character. The development of such pretreatment processes is expected to make the current biorefinery products more competitive, while concomitantly enabling the economic viability of other biorefinery routes for the production of new products of a biorenewable origin. Thus, the portfolio of chemicals and materials obtained from biorefinery schemes will be reinforced and expanded, improving the contribution of sustainable raw materials in the life cycle of the goods and commodities that we all use and consume as a society. This will be accompanied by the diminution of the atmospheric pollution that will result of replacing conventional organic volatile solvents with the non-volatile ionic liquids. In a similar vein, the non-generation of organic vapors by the ionic liquids will help to create safer and healthier environments for the workers in the corresponding biorefinery plants.

A better geodistribution of lignocelluloses, as compared to the current non-renewable sources, and their non-edible character, are additional characteristics that are expected to have a beneficial impact at a social level in a global context with the consolidation of the lignocellulosic biomass biorefinery paradigm.

Conflict of interest

There are no conflicts to declare.

Acknowledgments

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STUDIES ON THE INFLUENCE OF AlTi5B1 MODIFIER ON THE STRUCTURE AND PROPERTIES OF AlCuMg ALLOYS

Wojciech Ściężor*
AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Department of Metal Working and Psychical Metallurgy of Non-Ferrous Metals
30 Mickiewicza Av., Krakow, 30-059 Poland, wsciezor@agh.edu.pl
https://orcid.org/0000-0001-8974-5970

Radosław Kowal
AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Department of Metal Working and Psychical Metallurgy of Non-Ferrous Metals
30 Mickiewicza Av., Krakow, 30-059 Poland
https://orcid.org/0000-0003-0332-8493

Krystian Franczak
AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Department of Metal Working and Psychical Metallurgy of Non-Ferrous Metals
30 Mickiewicza Av., Krakow, 30-059 Poland
https://orcid.org/0000-0002-0135-3700

Justyna Grzebinoga
AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Department of Metal Working and Psychical Metallurgy of Non-Ferrous Metals
30 Mickiewicza Av., Krakow, 30-059 Poland
https://orcid.org/0000-0003-4890-7528

Paweł Kwaśniewski
AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Department of Metal Working and Psychical Metallurgy of Non-Ferrous Metals
30 Mickiewicza Av., Krakow, 30-059 Poland
https://orcid.org/0000-0002-7826-6672

Grzegorz Kiesiewicz
AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Department of Metal Working and Psychical Metallurgy of Non-Ferrous Metals
30 Mickiewicza Av., Krakow, 30-059 Poland
https://orcid.org/0000-0001-9518-5498

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Abstract

New materials used in various industries require sufficiently high mechanical properties, fine-grained structure and ease of metal forming while minimizing production costs. For this reason, work is being carried out to develop new groups of alloys that make it possible to increase the strength of the obtained components while reducing their weight, and thus reducing production costs. This article focuses on two aluminium-based alloys with different content of alloying additives: copper and magnesium i.e., AlCu3Mg3 and AlCu4.5Mg6, which were produced by metallurgical synthesis. The as-cast alloys were characterized for their basic physical, mechanical and electrical properties and were subjected to structural analysis. In the next stage, the alloys were modified with 100, 500, 1000 and 2000 ppm of titanium and then their hardness, electrical conductivity and density were tested. Samples were also subjected to microstructural analysis. The obtained results allowed to examine the evolution of the AlCuMg alloy properties depending on the content of alloy additives and the amount of used modifier.

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Keywords
aluminium, AlCuMg, modifier, AlTiB, casting

Introduction

Modern materials based on aluminium and other metals are faced with ever higher requirements in terms of their functional and operational properties, with a simultaneous tendency to reduce the weight and price of the final products. This is most often achieved by shortening the technological line of their production and reducing material consumption. Obtaining the required material properties is possible both through the development of a new range of alloy grades (determined by the selection of appropriate alloy additives) and the use of the best production technology for a given product and the path of further processing.

The idea and the main assumption of this work was to obtain new varieties of Al-Cu-Mg alloys by casting, constituting a specific combination of the 2XXX series (aluminium - copper) and 5XXX series (aluminium - magnesium) alloys, and to conduct research on the effect of modifier addition on the structure and final mechanical and electrical properties as well as the internal structure of the product.

Aluminium-copper alloys (series 2XXX) are a group of materials with high strength properties which are commonly subjected to heat treatment (supersaturation and aging, both natural and artificial). On the other hand, aluminium-magnesium alloys, despite the presence of the solvus line in their phase diagram (which allows for their thermal treatment), are mainly produced as solution-hardened alloys or by cold plastic deformation. The concept of obtaining new, high-strength alloys is therefore a combination of the advantageous properties of Al-Cu and Al-Mg materials. With the selection of the appropriate proportion of Cu and Mg in the alloy and their heat treatment, the new material will have a high set of mechanical properties based on the superposition of precipitation and solution hardening phenomena. The design of new types of materials should be correlated with the appropriate technology of their production.

The classic production technology of profiles made from aluminium alloys which are commonly known and used is based on the process of metallurgical synthesis and refining of liquid metal which allows to cast large-size ingots and cooling process (diameters of ingots are ranging from 200 mm to 300 mm). Next the process of long-term heating of ingots occurs (the so-called homogenization) and following cooling, reheating of the ingots for extrusion and the subsequent process of extruding the bars, homogenization and supersaturation and heat treatment (natural or artificial aging) is used. The alternative technology (proposed for the new group of AlCuMg alloys) is based on the process of metallurgical synthesis and refinement of liquid metal, continuous casting, homogenization annealing and supersaturation and heat treatment (natural or artificial aging). Its use allows for a significant shortening of the production line of products (round profiles) and the elimination of the most expensive process such: heating of ingots before the extrusion process and the extrusion process itself.

However, it should be noted that the final product from the extrusion process is characterized by a favourable, fine-grained internal structure, guaranteeing its high strength and ease of processing by metal forming. The structure of cast materials is completely different. For pure metals and alloys, the classic casting structure includes a frozen crystal zone at the surface, a dendritic zone and an equiaxed crystal zone around the axis of the ingot. However, this type of structure is not advantageous due to the low mechanical properties and susceptibility to cracking (during metal forming) of the obtained materials. An effective method of grain refinement and mechanical properties increase, used in practice, and derived from the theory of heterogeneous nucleation, is the control of the crystallization process. It is done by creating an appropriate base for crystal nucleation. Such procedure is called structure modification [1–3]. Increasing the number of grains in the material directly improves the mechanical properties and, what is extremely important, reduces the segregation degree and susceptibility to hot cracking of alloys [4].

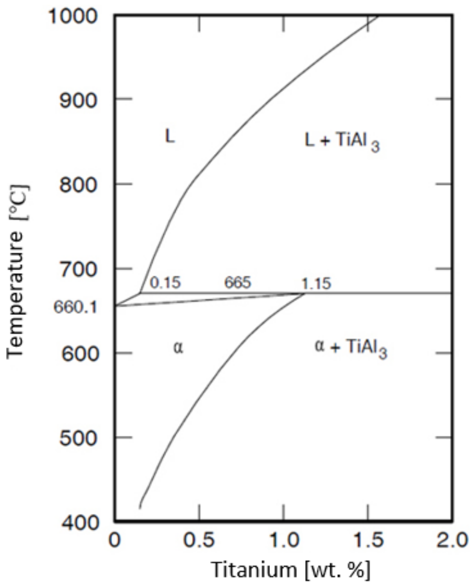


Fig.1.The aluminium rich side of the Al-Ti phase diagram *[5]*

Titanium was used as the first modifier for aluminium and its alloys. The addition of Ti increases the melting point to 665 °C. This effect is essential for the nucleation and growth of solid aluminium grains. The titanium additives are introduced by aluminium master alloys containing numerous crystals of the TiAl3 compound. From the relationships depicted in the Al-Ti phase diagram, a Ti-rich metal in contact with aluminium may start to solidify at a temperature that is above the melting point of the base alloy. Hence, the first solid phase nucleation will start near the surface of the AlTi3 particle [5]. Nevertheless, there is a disadvantageous phenomenon in the process - the decomposition of TiAl3 particles, which leads to the disappearance of the grinding effect and it is necessary to supply the process with high amounts of master alloys to maintain this effect. Therefore, intensive research led to the creation of Al-Ti-B master alloys. Most of the titanium in modern modifiers is present as TiB2, which is practically insoluble in molten aluminium, so high amounts of such master alloys are not necessary. When it is used, there is also a long-lasting fragmentation effect [6]. In industrial practice, research was also carried out on the use of Al-B alloys as a substance disintegrating the structure [7]. It turned out that AlB2 is a very efficient modifier, but it dissolves readily in aluminium, where it reacts with titanium and strontium in the alloy. Additionally, it deteriorates the susceptibility of the alloys to metal forming, causing their brittleness [8]. Further research led to the observation that TiB2 particles also had some disadvantages. They are quite thick and tend to agglomerate, which creates many quality problems with the final products. This contributed to the development of Al-Ti-C master alloys. Even though TiC particles are smaller and less prone to agglomeration than TiB2, they have not gained such widespread use as TiB2. The main reason was their low efficiency [7,9]. The above-mentioned problem of modification of aluminium and its alloys is described in the literature. However, there are no in-depth analyses of the behaviour of the material after casting, with a high content of such alloys as Cu and Mg, and thus constituting the research material that is the subject of this study. On this basis, a decision was made to test the influence of the most promising structure modifier (according to the authors) [6] - the effect of AlTi5B1 master alloy modification on the properties and structure of AlCuMg alloys dedicated to the continuous casting process and direct processing by metal forming (mainly die forging) and machining.

Methods

Melting, metallurgical synthesis and casting of individual alloys were carried out in order to obtain materials for testing. First, the material for casting was prepared, both in the form of pure aluminium and alloy additives such as pure magnesium (100%), AlCu50% master alloy and AlTi5B1 structure modifier. The base material (99.7% pure aluminium) in the form of pieces was placed in a crucible mounted in an induction furnace, which was heated to a temperature of 740 °C. After the pure aluminium was melted, the alloying additives (Mg and AlCu50%) were introduced into each crucible. Next metal was thoroughly mixed and left in the furnace for another 10 minutes.

After melting and mixing the components, Desydral (in the amount of 0.5% of the feed weight) was added using a special graphite lance to degas the alloy. The liquid metal refining process took 3 minutes in total. In the final stage of alloying, the alloy was refined with argon gas (refining time of 5 minutes). The exact amounts of the input materials, master alloys, modifiers and refining agents used are shown in Table 1.

Table 1. Mass of each input material used in the metallurgical synthesis process

Alloy	Mass of individual input materials [g]				
	Al	Mg	AlCu50	AlTi5B1	Desydral
AlCu3Mg3	250	7.5	15	0	1.36
AlCu3Mg3 + 100ppm Ti	250	7.5	15	0.55	1.36
AlCu3Mg3 + 500ppm Ti	250	7.5	15	2.73	1.36
AlCu3Mg3 + 1000ppm Ti	250	7.5	15	5.45	1.36
AlCu3Mg3 + 2000ppm Ti	250	7.5	15	10.90	1.36
AlCu4.5Mg6	230	10.4	27.6	0	1.34
AlCu4.5Mg6 + 100ppm Ti	230	10.4	27.6	0.54	1.34
AlCu4.5Mg6 + 500ppm Ti	230	10.4	27.6	2.68	1.34
AlCu4.5Mg6 + 1000ppm Ti	230	10.4	27.6	5.36	1.34
AlCu4.5Mg6 + 2000ppm Ti	230	10.4	27.6	10.72	1.34

Afterwards, the crucibles were removed from the furnace, mixed again to homogenize the material in volume and poured into a crucible with an internal diameter of 40 mm and a height of 120 mm. The material in the form of ingots was obtained, from which samples were cut for further tests. As a result, alloys with the following chemical composition were obtained: AlCu3Mg3 and AlCu4.5Mg6. Obtained castings were analysed for their basic physical, mechanical and electrical properties, which allowed to obtain information about the properties of these alloys in the state after casting and before modification (reference material). The other part of the castings obtained by metallurgical synthesis was modified with titanium in the form of AlTi5Bi master alloy with Ti 100, 500, 1000 and 2000 ppm. Fig. 2 shows the process of metallurgical synthesis of castings.

Fig.2. Stages of the Al-Cu-Mg metallurgical synthesis (a-pure aluminium, b –melting a batch in an induction furnace, c – refining of the liquid metal, d – ingot and samples taken for testing from Al-Cu-Mg alloy). *Source: Authors'*

Finished ingots made of AlCuMg alloys were tested for physical, mechanical and electrical properties after casting and after modification. Before starting the tests, samples were cut from the central part of each casting and polished with sandpaper with a grain size of 500, 800, 1200, 1500, 2000, respectively.

The hardness tests were carried out using the Brinell method. Analysis was carried out on an INNOVATEST model NEXUS 3000 hardness tester with a ball with a diameter of 2.5 mm and at a given load 31.25 kg. Five prints were made on each of the samples.

After the hardness test, electrical conductivity was measured on the same samples, 10 measurements were made on each of the samples. The electrical conductivity was measured with a Sigmatest model 2.069 meter, using the eddy current method.

Another study which was carried out was the measurement of the casting density, based on the Archimedes law, the density was determined using the following relationship:

$$\rho = \frac{m_p}{m_p - m_w}\left(\rho_w - \rho_p\right) + \rho_p$$

where:

ρ – density of the tested material [g/cm^3],
m_p – mass of the tested sample in the air [g],
m_w – mass of the tested sample in the water [g],
ρ_p – air density [g/cm^3],
ρ_w – the density of distilled water at a certain temperature [g/cm^3].

Density of distilled water was determined based on tabular data which links it with test temperature. The obtained final density result was the average of five individual measurements.

As part of the work, microstructural tests were also carried out using the Olympus GX 51 light microscope equipped with digital image recording.

Results and discussion

At the first stage of the research, the Brinell hardness measurements were carried out on AlCu3Mg3 and AlCu4.5Mg6 alloys in the state immediately after casting and after modification with titanium. The results of hardness measurements are presented in Fig. 3.

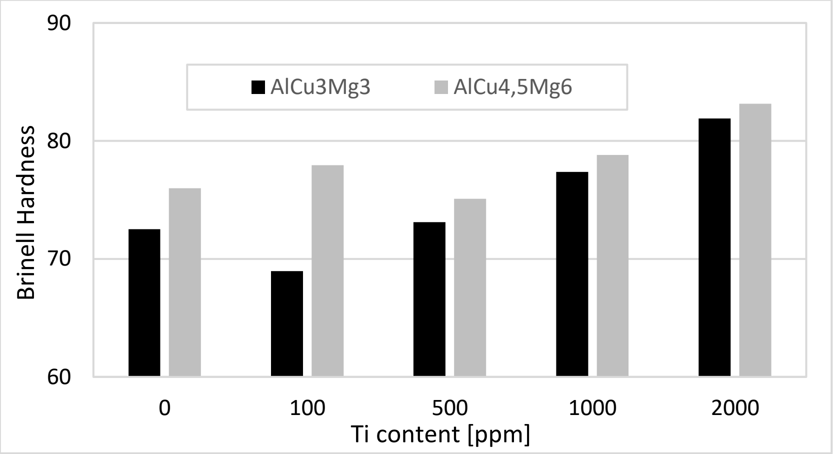


Fig. 3. Brinell hardness for samples with different titanium content.

Source: Authors'

The AlCu3Mg3 and AlCu4.5Mg6 alloys in the condition after casting have Brinell hardness of 72.5 and 76 HBW, respectively. Mechanical properties of the examined alloys in the as-cast state show significant increase in the hardness compared to alloys described in the literature. According to the research results presented in [10], AlCu alloys with the content of copper addition at the level of 2% and 4% by weight show a hardness of 37 and 47 HBW respectively, while the AlCu4.5 alloy in the state after casting reaches a hardness value of 57 HBW [11]. AlMg alloys with a level of magnesium 3% and 6% have hardness of 58 and 60 HBW respectively [12]. The obtained results of hardness measurements of the tested AlCuMg alloys are at a satisfactorily high level already at the casting stage.

The titanium modification of the AlCu3Mg3 alloy results in an increase in the hardness of the alloy, reaching the highest hardness for a Ti-modified sample in the amount of 2000 ppm, which is a 13% increase in hardness compared to the sample after casting. Slightly lower hardness in relation to the casting hardness was recorded for the AlCu3Mg3 sample enriched with the modifier in the amount of 100 ppm (69 HBW - hardness decrease by 5%), which may be caused by different structure in relation to other samples or local porosity of the material. Modification with titanium in the amount of 500 and 1000 ppm increased the hardness in relation to the casting by 1 and 7% respectively.

AlCu4.5Mg6 alloy has a hardness of 76 HBW in the as cast state. Hardness is increasing with increasing the amount of modifier. The highest hardness has a sample with the addition of a modifier in the amount of 2000 ppm – 83.1 HBW (hardness increase by 9% compared to the alloy before modification). The addition of titanium in the amount of 100 and 1000 ppm increased the hardness of the alloy by 3 and 4%, respectively. Modification of titanium in the amount of 500 ppm decreased the hardness in relation to casting by approx. 1%.

The results of the electrical conductivity tests of AlCuMg alloys in the as-cast state and after modification with various titanium contents are shown in Fig. 4.

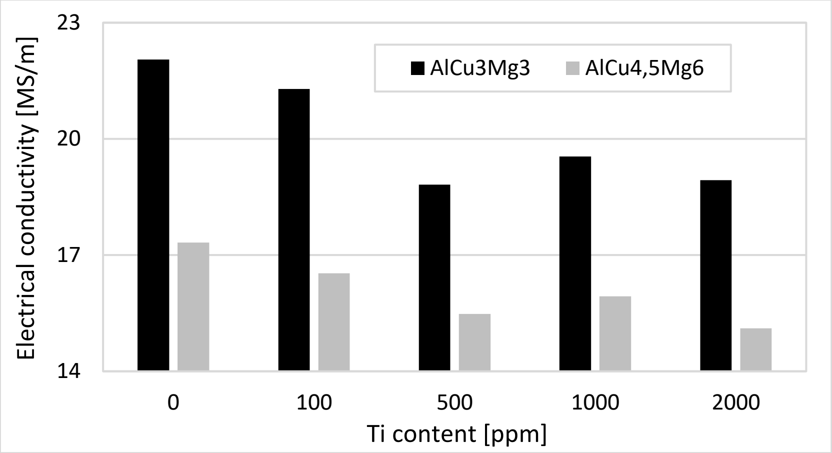


Fig. 4. Electrical conductivity for samples with different titanium content.
Source: Authors'

As a result of modification of AlCuMg alloys, a decrease in their electrical properties was observed. The AlCu3Mg3 alloy generally has better electrical properties than the AlCu4.5Mg6 alloy, both as-cast as well as after modification. It is related to the lower content of copper and magnesium alloying additives, which reduce the electrical properties of the material.

The AlCu3Mg3 alloy in the as-cast condition shows electrical conductivity of 22 MS/m. The lowest level of electrical properties was obtained when the alloy was modified with titanium in the amount of 500 ppm (18.8 MS/m) and 2000 ppm (18.9 MS/m) which results in a decrease of the electrical conductivity of the alloy by 15 and 14 % respectively.

Before modification, the AlCu4.5Mg6 alloy shows electrical conductivity of 17.3 MS/m, decreasing in electrical properties to the level of 15.1 MS/m for the modification with titanium in the amount of 2000 ppm (a decrease in electrical conductivity by 13%). It is directly related to the increase in the number of grain boundaries in the material. Modifier addition reduces the electrical conductivity of the casting by 5% (100 ppm Ti), 10% (500 ppm Ti) and 8% (1000 ppm Ti).

As part of the research, the density of the samples was also measured. Results are shown in Fig. 5.

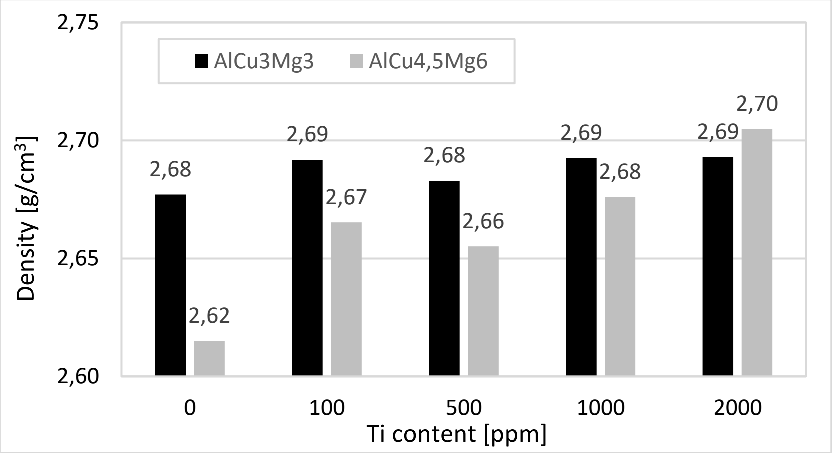


Fig. 5. Density of samples with different titanium content.
Source: Authors'

The density of the tested castings before modification was 2.68 g/cm^3 for the AlCu3Mg3 casting and 2.62 g/cm^3 for the casting with a higher content of alloy additives (AlCu4.5Mg6).

In case of AlCu3Mg3 alloys, the density does not change significantly with increasing titanium content, oscillating around 2.68-2.69 g/cm^3. In case of the AlCu4.5Mg6 alloy, there is a noticeable variation between individual samples. The highest density has a sample with a titanium content of 2000 ppm equal to 2.70 g/cm^3, and the smallest density has a sample directly after casting – 2.62 g/cm^3, which proves the beneficial effect of the modification treatment on reducing the porosity of the castings.

Industrial AlMg alloys dedicated for metal forming have density in the range of 2.64-2.69 g/cm^3 [13]. 2XXX series aluminium alloys show a slightly higher density at the level 2.75-2.84 g/cm^3 [13]. According to the literature data, the density of AlCu alloys with the addition of copper in the amount of 2% and 4% by weight is at the level of 2.72 and 2.77 g/cm^3 respectively, and the alloy density increases with increasing copper content [10]. The introduction of the modifier to the examined AlCuMg alloys allows to obtain a density which for the tested alloys is similar to pure aluminium (2.70 g/cm^3), therefore conclusion is that these products do not show significant porosity [13].

Structural tests were also carried out on the prepared samples. They included the analysis of the microstructure using an optical microscope. The obtained microstructures are shown in fig. 6-9.

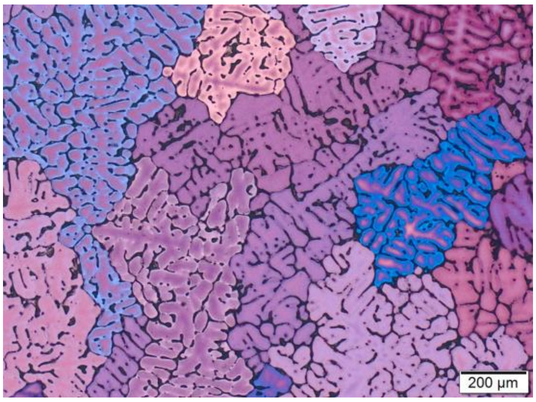
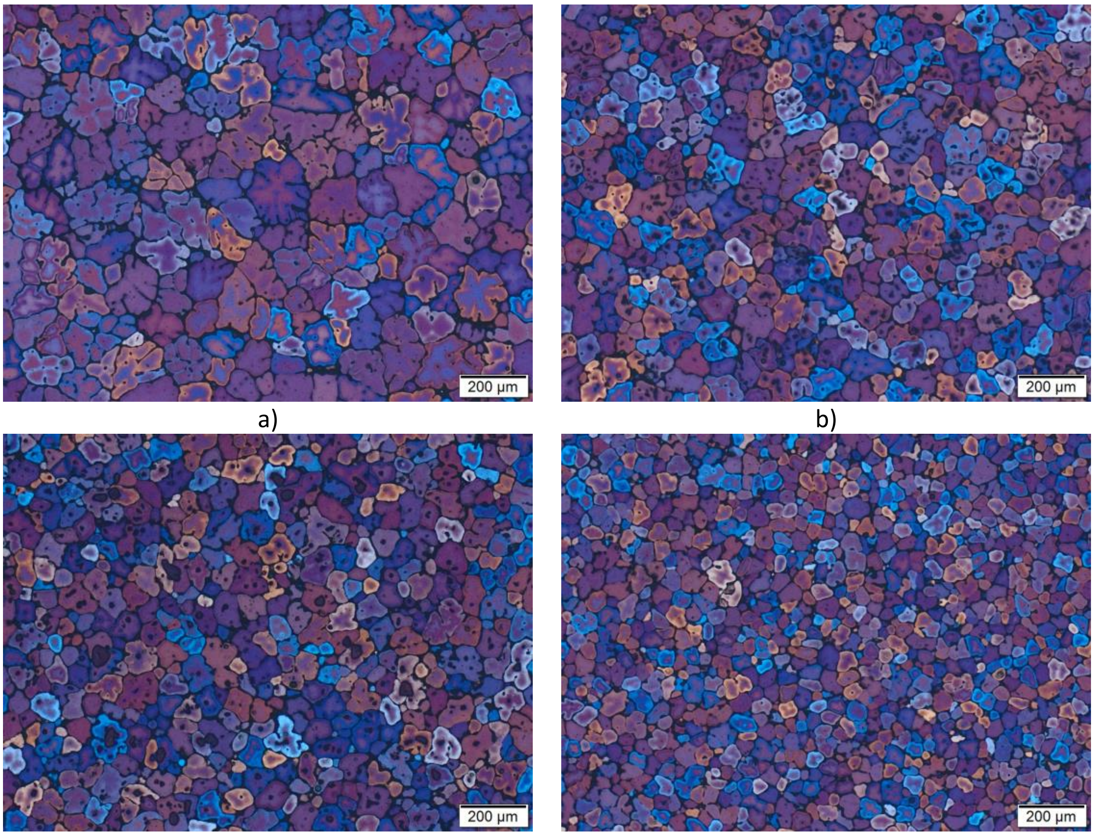


Fig. 6. Microstructure of AlCu3Mg3 alloy before modification.
Source: Authors'



a) b)

c) d)

Fig. 7. The microstructure of AlCu3Mg3 alloys modified with various titanium content: a) 100 ppm b) 500 ppm c) 1000 ppm d) 2000 ppm. *Source: Authors'*

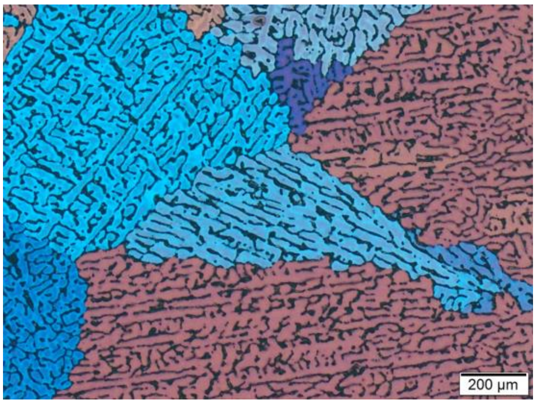
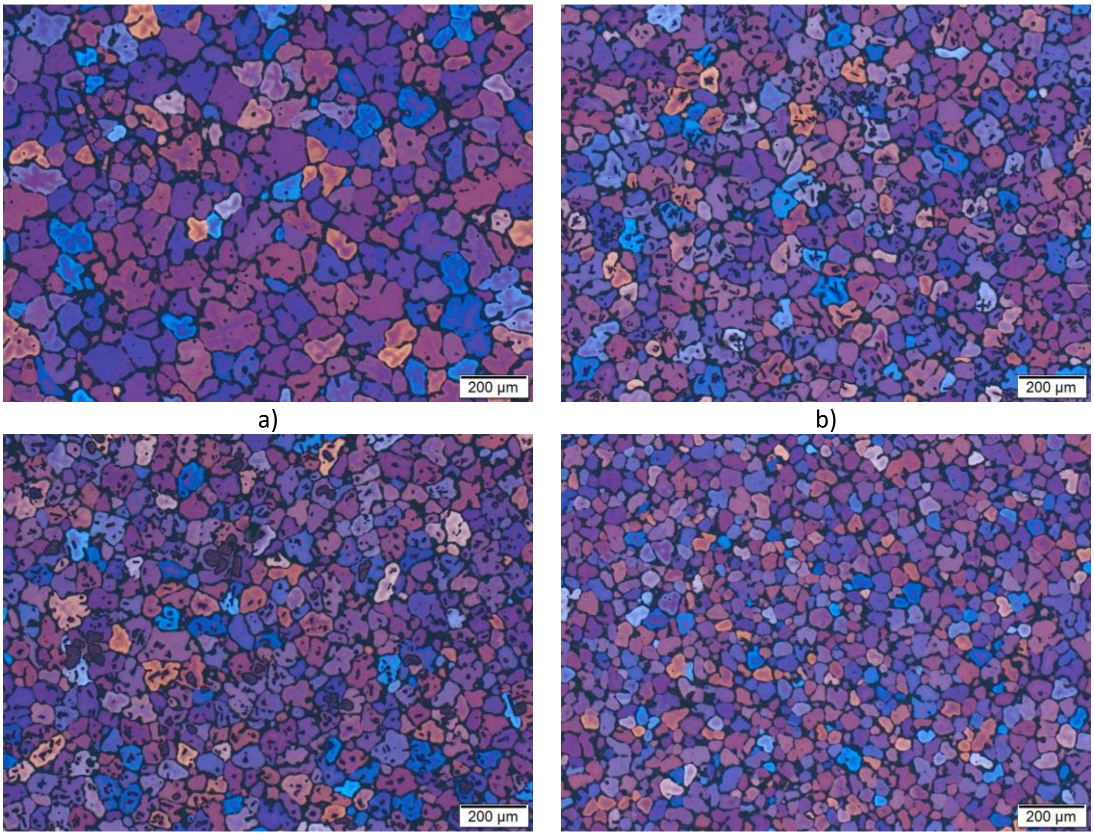


Fig. 8. Microstructure of AlCu4.5Mg6 alloy before modification.
Source: Authors'



a) b)

c) d)

Fig. 9. Microstructure of AlCu4.5Mg6 alloys modified with various titanium content: a) 100 ppm b) 500 ppm c) 1000 ppm d) 2000 ppm. *Source: Authors'*

Before modification AlCuMg alloys had a classic casting structure, the distribution of grains in the cross-section was rather irregular and their size reached a few or even several millimetres. The addition of the modifier in the amount of 0.1% resulted in significant grain fragmentation in the ingots to a diameter of about 0.1-0.2 mm. Such a small amount of modifier contributed to the satisfactory refining effect of the ingot structure. Increasing the titanium content in the alloy contributed to the reduction of the grain diameter by approx. 0,1 mm and less for 500 - 1000 ppm Ti. The addition of titanium in the amount of 2000 ppm led to a very fine fragmentation of the structure of the ingot. The grains had a diameter of approx. 0.05 mm and less. The tested scope of titanium addition in castings has a positive effect on the structure and grain diameter reduction. The obtained grain size corresponds to products extruded from aluminium alloys [14,15].

The modification treatment contributed to the transformation of the structure from columnar grains (dendrites) to equiaxed grains as well as to the reduction of grain size (with a simultaneous increase in their amount), which improves their ease of metal forming and contributes to a reduction in costs and improvement of production efficiency [4]. Reducing the grain size in ingots is one of the strengthening mechanisms according to the Hall-Petch relationship [16]:

$$\sigma_p = \sigma_0 + kd^{-1/2}$$

where:
σ_p – yield point,
σ_o – constant,
k – constant,
d – average grain size.

Increasing the number of grains because of the modification treatment contributes to a direct improvement of mechanical properties (low for pure aluminium) and a reduction in the degree of segregation and susceptibility to hot cracking of the alloys.

Impact

There is a constant market demand for new products obtained from new types of alloys in innovative, cost-effective manufacturing technologies. This is especially true within non-ferrous metals market where year-to-year there is an intensive substitution of extremely expensive copper products with products based on aluminium and its alloys. Various AlCuMg alloys subjected to tests constitute a specific combination of the 2XXX AlCu series and the 5XXX AlMg series. These alloys will have up to 10% higher mechanical properties (after heat treatment) than the current alloys of the 2XXX series. This type of product (round cast profile) with higher properties, used for products obtained in the further processing by die forging or machining, will allow for direct replacement of some of the existing alloys and partial reduction of weight and dimensions ("sliming") of the final products, since the "slimmed-down" product, thanks to its higher strength properties, will be characterized by a load capacity comparable to the products currently used. Limiting the mass of the product brings measurable economic benefits (lower product price) resulting from lower material costs of production. It should also be remembered that the profiles currently used for the die forging process and machining are made of 2XXX, 5XXX series alloys, which are obtained in traditional technology - the extrusion process and a number of accompanying operations that are energy and material consuming (the issue of production waste). The proposed technology of continuous casting of products from new varieties of AlCuMg alloys will therefore allow for a partial reduction of the product price also at the production stage.

After assuming market prices of pure metals such as aluminium, copper and magnesium, as well as knowing the costs of acquiring metallurgical master alloys (AlCu50 and AlTi5B1), taking into account employee costs, electricity, heat treatment and other costs determined based on conversations with entrepreneurs from the industry casting and metal forming of non-ferrous metals, it can be estimated that the cost of producing 1 kg of profile extruded from the currently used 2XXX series alloys is approximately 10.7 PLN/kg. The production of the same amount of profile from the new range of AlCuMg alloys based on the continuous casting technology will reduce this price to approximately 9.85 PLN/kg. Additionally, the production costs can be reduced by about 13% (to the level of 8.7 PLN/kg) in case of using 80% of the total input for the foundry process as the input material of qualified waste materials (scrap). Obviously, the amount of scrap can be increased up to 95%, which will additionally reduce the cost of manufacturing the product.

The reduction in the price and the fact that the final forging or machined parts can be slimmed down by about 5-10% (which will result in a reduction in the material consumption of the product) allows to state that the work covered by this study a significant impact and a favourable economic effect. It also allows for the management of a large part of waste scrap from non-ferrous metals.

Conclusions

The basic physical, mechanical, electrical and structural properties on a micro scale were tested on new aluminium-based alloys with various contents of copper and magnesium alloying additives, which underwent a structure modification treatment. Modification with the use of inoculants is aimed at changing the form of the casting structure - from the classic casting structure to a fine-grained and uniform structure over the entire cross-section of the ingot. This type of alloy structure has a positive effect on the mechanical properties and the ease of metal forming processes. Analysing the results obtained in the experimental tests, a significant influence of the addition of the structure modifier in the form of titanium on the mechanical, electrical and structural properties of Al-Cu-Mg alloys is noticeable.

The hardness of the alloys after casting reaches a higher value for the alloys with a higher content of AlCu4.5Mg6 alloying additives than for the AlCu3Mg3 alloys. The addition of titanium significantly increased the hardness of the castings after the modification in relation to the hardness of the alloy after casting. After the Brinell hardness test, the highest increases were obtained for titanium content of 2000 ppm for both the AlCu3Mg3 alloy (13% increase) and the AlCu4.5Mg6 alloy (9% increase in hardness). Generally, a greater impact on the hardness of the alloy because of modification with titanium with different additive content was observed for the AlCu3Mg3 casting. The hardness increase is higher than for the analogous modification variants in case of the AlCu4.5Mg6 alloys. The hardness test being the measure of the mechanical properties of the casting clearly indicates the positive effect of the modifier on the increase in strength properties of AlCuMg alloys.

The electrical conductivity of the alloys in the as-cast condition reaches the level of 22 MS/m for the AlCu3Mg3 alloy and 17.3 MS/m for AlCu4.5Mg6 alloy. The modification treatment contributed to the decrease in the electrical properties of the alloys, the highest decrease to 18.8-18.9 MS/m (14-15% of the electrical conductivity value before modification) was recorded for the modification of the AlCu3Mg3 alloy with titanium in the amount of 500 and 1000 ppm. The decrease in electrical properties of 13% was observed after modification of the AlCu4.5Mg6 alloy with titanium in the amount of 2000 ppm. According to the literature data, the addition of titanium, even in small amounts, reduces the electrical properties of aluminium, which is also confirmed by the results of the research.

The study of the density of the alloys before and after the modification showed no significant differences for both alloys, reaching the same density level for the AlCu3Mg3 alloy with different titanium content, while for the AlCu4.5Mg6 alloy there was a slight differentiation in the density levels of ~ 0.08 g/cm^3 which proves the positive effect of the modification on reducing the porosity of the alloy. The density of AlCuMg alloys enriched with titanium is similar to that of pure aluminium, which proves the beneficial effect of the modification treatment on reducing the porosity of the castings.

To sum up, the tested alloys already at the casting stage have high mechanical properties, which will be even higher after applying heat treatment. The use of the structure modifier allows for their additional increase and most importantly, the reduction of the average grain size to the size known from traditionally used extruded products. Their advantage is that they are obtained in the continuous casting technology, which means that they will be significantly cheaper than those currently offered on the market. Additionally, they can be made from aluminium scrap, which may further reduce the price of the final product.

Conflict of interest

There are no conflicts to declare.

Acknowledgments

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LIFE CYCLE ASSESSMENT AS TOOL FOR REALIZATION OF SUSTAINABLE DEVELOPMENT GOALS - TOWARDS SUSTAINABLE FUTURE OF THE WORLD: MINI REVIEW

Joanna Bojarska*
Institute of General and Ecological Chemistry, Lodz University of Technology, Faculty of Chemistry
Żeromskiego 116, Lodz, 90-924, Poland, joanna.bojarska@p.lodz.pl
https://orcid.org/0000-0001-9190-6913

Patrycja Złoty
Institute of General and Ecological Chemistry, Lodz University of Technology, Faculty of Chemistry
Żeromskiego 116, Lodz, 90-924, Poland

Wojciech M. Wolf
Institute of General and Ecological Chemistry, Lodz University of Technology, Faculty of Chemistry
Żeromskiego 116, Lodz, 90-924, Poland
https://orcid.org/0000-0002-9162-9933

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Abstract

“One planet, one main goal: good life for all”: it could be a motto of sustainable world. Sustainability is global mega trend in all fields of life to promote prosperity protecting our planet. Sustainable development is a requirement and a priority for all people all over the world. It is defined as development of the current world with a view to the future generations. In 2015, the UN Member States established Agenda 2030, including seventeen “Sustainable Development Goals”, SDG, which should be realized by 2030. Objectives scope all areas of life, namely quality of human life, ecosystem, world peace or partnerships. Each goal has an environmental context. According to the “United Nations Environment Program” (UNEP), Life Cycle Assessment (LCA) is a perfect method in the context of the environmental dimensions of the SDGs. The concept not only concerns the effects of the process/production system or the product/service but also all stages of its life (from cradle to grave), considering the carbon, environmental, consumer or biodiversity footprints. LCA is the only comprehensive eco-innovation indicator and policy implementation technique of sustainable development in companies in terms of eco-efficiency and eco-products. This mini review provides a survey of the current state of knowledge on sustainability and sustainable development as well as the relevance of new holistic methodology bridging SDGs with LCA, on the base of the newest scientific worldwide literature.

Keywords

Sustainability, sustainable development, methodology: Life Cycle Sustainable Assessment (LCSA), Sustainable Development Goals (SDGs)

Introduction

Our age is called *Anthropocene* defining by climate change, fast loss of biodiversity and natural resources. Nowadays, civilization, massive consumption, continuous development of industry and economy leads to very bad condition of our planet. Consequently, not only environmental but also economic and social dysfunctions cannot be overlooked [1,2]. Therefore, sustainability in all aspects of our life is necessary. Sustainable Development Goals (SDGs), established by all United Nations Member States, are a priority for sustainable development of the world, to improve quality of our planet, human life in all countries worldwide now and in the future [3]. This mini review is focusing on the state-of-the-art of diverse aspects of sustainability and sustainable development as well as its challenges and methodological approaches for the assessment of the sustainability. In this context, Life Cycle Sustainability Assessment (LCSA), should be highlighted as the most suitable tool helpful in the achievement of ambitious sustainability targets, considering potential applications of bridging this holistic method with SDGs. Briefly speaking, the concept of LCSA is based on the Life Cycle Thinking (LCT), directing thinking towards protection of ecosystem and shaping pro-ecological citizenships. LCSA is combing of environmental (Life Cycle Assessment - LCA), economic (Life Cycle Costs – LCC) and social (Social-Life Cycle Analysis - S-LCA) models of life cycle analysis.

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LCA is standardized analytical method in the terms of combination and assessment of the inputs, outputs and potential impacts of products on environment in their life cycle, LCC takes into account all costs during the life cycle, while S-LCA includes social features related with entire life cycle. All of them are described in detail in the section entitled Results.

Our aim was directed into answering the main question - if this method is helpful and sufficient to realization ofSDGs and identification other eventual useful tools and gaps in the scientific studies. More specifically, this mini-review provides an overview of the definition, evolution, scope, importance of sustainability for protection our planet and improving quality of life in relation to current and future generations, as well as development ofmethodologies used to realise sustainable targets. The main objectives of this paper are thorough survey of the scientific literature fulfilling the following certain criteria:

- clarifying definitions of sustainability, sustainable development and description of their evolution over the years,
- understanding the most important issues in the aspect of sustainable development,
- characterization of sustainable goals including identification of their main common context,
- -recognition among available tools useful in either qualitative or quantitative interpretation of results concerning environmental impacts of products/processes/organisations in the context of their life cycle,
- evaluation of the state of knowledge on the particular topics related to methodological concepts, identification their advantages and disadvantages, and gaps in the scientific literature, to formulate future research possibilities towards technical improvements.

Overall, the findings revealed that concept of Life Cycle Sustainable Assessment (LCSA) is the best complex strategy capable of integrating essential aspects leading to assessment of impacts on ecosystem during the entire life cycle and combining LCA with sustainable assumptions. Nevertheless, current method does not include sufficient data integrating all dimensions of sustainable goals. Therefore, future technical development into proposed novel LCA -SDGs methodology should put more emphasis on introduction into databases and calculations as many factors as possible providing holistic evaluation in terms of all sustainable goals. This mini-review is the first, on the best of our knowledge, on this range of main topic, consequently providing novelty into the LCSA state-of-the-art knowledge. More specifically, only materials of PRé-Sustainability company, which is working on new methodology, are available. In the scientific literature, suitable articles are lacking. Papers concerning LCSA aspects and selected issues of possible linking LCA with SDGs can only be found. We tried to examine the validity and accuracy of new proposed LCA-SDG technique on the base of collected all published information. Broadly speaking, this work may serve as background for further studies suggesting future directions.

The rest of the paper is organised as follows: methodological approach to literature overview, discussion of results of literature survey, including important issues in the range of topic, summary, impact and conclusions.

Methods

This article has character of usual mini-review focusing on the newest scientific articles scattered across the world literature. More specifically, the review process has been performed in the below described manner:

The first step towards planning the paper was directed to basic research questions. The overview is concerned about the relevance of global sustainability development in protection our planet, and innovative methods helpful in realization of sustainable goals. In this context, the three main research questions, are as follow:

- what is the reason, the characteristic landscape and result of sustainable development in a wider perspective?
- what are sustainable goals?
- what are the main techniques helpful in realisation of the global targets?

As regards the subsequent stages of review strategy, the expressions used to survey of suitable articles were: sustainability, sustainable development, Life Cycle Sustainable Assessment (LCSA), Sustainable Development Goals (SDGs).

We searched scientific articles, especially from the five last years since Sustainable Goals were reported. Next, for wider perspective and collection all available data, we included conference papers and other materials as well, published either in English, German or Polish. The actual data were the most interesting and important. Nevertheless, for deeper background and evolution of sustainability, we included papers published over the previous centuries as well.

The next step was collection of all information on new promising methodology combining LCA with SDGs. In this case, we extended literature survey to additional materials published mainly by PRé-Sustainability company, The Netherlands (but also OnePlanet and LCA Consultant), which is working on new methodology. Unfortunately, non-scientific key articles are visible. Therefore, we did not limit scope of literature survey. All kind of information (presentations, reports, bulletins etc.) published on the websites of this company were very valuable for preparing appropriate review. However, it should be highlighted that even such information is very rare.

To sum up, we used different web browsers. Nevertheless, mainly the Scopus database was helpful in the context of collection of scientific articles.

Results and discussion

Sustainability

The term "sustainability" (*sustinere* in Latin) means "to hold" (sub, under) in relation to improving quality of life with care for environment. The roots of this expression can be tracked back to the antiquity and the world of hunting [4,5]. Originally, sustainability was defined only in the context of effective use of natural resources by people in the long term. Its concept (*Nachhaltigkeit* in German) was applied to German forestry industry, in the 18th century [6,7]. In the book of Hans Carl von Carlowitz from Freiberg (in Saxony), entitled "*Sylvicultura Oeconomica* (or the *Economic News and Instructions for the Natural Growing of Wild Trees*), published in 1713, is described sustainability in the context of management and use of forests [8].Furthermore, in another publication, *Instructions for the Taxation of Forests,* written by Georg Ludwig Hartig (from Gladenbach) in 1804, is also pointed that forest industry is based on the sustainability [7]. Nowadays, sustainability has more complex meaning in the context of climate, environment, economic and human development focusing on progress, responsibility, freedom and culture in sense of respect for nature [9]. Maxim of sustainability is "*living off the interest rather than the capital".* Interestingly, Switzerland was the first country which introduced the expression "sustainability" to its constitution. In the article 2 we can read *"the Swiss Confederation supports the common welfare, the sustainable development, the internal cohesion and the cultural diversity of the country*" [6].Sustainability can be considered in different aspects: welfare either people or other living organisms, in terms of relationship between current and future generations [10]. Sustainability is very popular trend all over the world in all fields of life. Therefore, sustainability science has been developed [11]. The problems of sustainability and identification of solutions helpful in achievement of sustainable development are the main challenge in this field. Sustainability is "life principle" in terms of responsibility for either people currently living or future generations [7,12]. It is either a mission or a survival strategy.

Sustainable development

The 21st century is the century of sustainable development [13]. Sustainability should be considered in the terms of synergy of human life and ecosystem quality, while sustainable development is the holistic approach, covering economic welfare, social equity and environmental quality, leading to resulting points of sustainability [14]. Sustainable development consists of two essential issues: development and sustainability. According to the dictionary, development is "*the process in which someone or something grows or changes and becomes more advanced*", while sustainability is "*the quality of being able to continue over a period of time*". The latter, in the environmental context is defined as "*the quality of causing little or no damage to the environment and therefore able to continue for a long time*". Sustainability development can be expressed as economic development, while caring for the environment in relation to present and future generations [15–18]. In other words, it is sustainable improvement of living standards of people all over the world with care for natural resources, state of our planet, in the context of responsibility for future generations [19]. Notably, concept of sustainable development comes from economics [20]. Interestingly, the first consideration on limited natural resources for increasing population of people, started in the 1800s (Malthusian population theory) [21–24]. The need to sustainable development appeared together with the Industrial Revolution. Nevertheless, the first official declarations in the relation to sustainable development were in 1973, on the Congress entitled "*Growth and Its Implication for the Future*" [25] In 1980, term "sustainable development" was officially introduced, and described as a global priority [26,27].

Sustainable development focuses on the balance among economic prosperity, protection of biosphere and quality life of people [28,29].We should remember that either our survival or life of the future generation depends on responsible behaviour of all of us. Sustainable development is the key to a future better world [23,30]. The main principle is "*predict and prevent*".

Interestingly, in the Polish legal system, in the article 5 of The Constitution of the Republic of Poland we can read: *"Poland … ensures freedom, human rights and the security of citizens … it ensures environmental protection on the basis of sustainable development"…. "In order to achieve sustainable development, states should: reduce or eliminate patterns of production and consumption that disrupt these developments, develop scientific knowledge in this area, and effectively ensure that everyone has adequate access to it information on environment and raise public awareness in this area"* [31].

Sustainable Development Goals

In 2000, the eight Millennium Development Goals (MDGs) were established. The headline target was the improvement of health, poverty, gender and social aspects. Nevertheless, the focus was on the environmental sustainability [32]. It was discussed at the Conference on Sustainable Development (Rio Earth Summit 2012). In consequence, it led to improved and extended Sustainable Development Goals (SDGs) [3,33,34]. In 2015, Agenda 2030 for sustainable development has been established, leading to better human life and ecosystem quality. The seventeen SDGs (including 169 targets and 230 indicators [35] should be realized to 2030. The goals, listed in the Figure 1, are a roadmap and a call for all countries all over the world to the sustainable decisions and actions [35,36]. Notably, each aim has an environmental context.

Fig.1.Sustainable Development Goals [36]
Source: https://www.un.org/sustainabledevelopment/sustainable-development-goals/

Life Cycle Sustainability Assessment

Everything in nature has its own life cycle, from birth to death, namely man, animal or plant. Businesses, policies, technologies as well as products also have a life cycle in diverse meanings. In the latter case, life cycle consists of the following levels: introduction, growth, maturity, decline. According to the ISO, life cycle includes the corresponding stages of the production, from introduction of raw materials into processes to the final disposal/recycling of the product [37,38]. The concept of Life Cycle Thinking (LCT) focuses on the thinking about impact of everyday life to the environment in a holistic sense. We should be mindful of the fact that our behaviour, especially consuming products affects our planet. LCT is helpful in sensible decisions and actions leading to the reduction or elimination of negative impacts on the ecosystem and increase of the economic benefits within the entire life cycle [3]. Based on LCT, Life Cycle Management (LCM) and Life Cycle Sustainability Analysis (LCSA) were built to introduction of sustainable development-based knowledge useful in products' decision-making processes [39–42]. LCM is a management approach improving products/services within their life cycle. It is a manner of operationalizing sustainability in organizations (industrial and service sectors), concentrating on internal operations, costs or risk management. From the holistic point of view, we can say about Life Cycle Sustainability Management (LCSM [43]. Three main aspects of LCM are following strategies: environmental – knows as Life Cycle Analysis, or as Life Cycle Assessment (LCA), economic – Life Cycle Costs (LCC) and social – Social-Life Cycle Analysis (S-LCA). Bridging all of them leads to Life Cycle Sustainability Assessment (LCSA) [44–47]. LCSA is a balance among environmental, social and economic dimensions of sustainability. All these methodologies are based on the ISO 14040 standards [38].LCC is resulted to quantification of all costs during the life cycle (development, service, utility and recycling costs) [48], while S-LCA focuses on the social impacts over life cycle [49]. The latter is a method used for collecting and analysing data concerning real and potential socio-economic features related to products, processes and services within their life cycle[50]. LCA is analytical technique focusing on the identification, quantification and evaluation of the environmental impacts of a product/process/organization/man/service/activity in its all life cycle, from cradle to grave. Additionally, more circular aspect is considered, from cradle to cradle - in the case of product recycling (and its "new life") [41]. Therefore, all life phases are included into analysis. In the case of product, it is extraction of raw materials, production, transportation, storage, use stages, recovery, reuse and disposal. Comparison of real and potential impacts of diverse products are also possible [51,52]. The concept of LCA has its roots in the 1960s in relation to packaging studies and energy use in the US and Northern Europe, in cooperation of universities and industry. The first results, related to energy requirements to produce chemicals, were presented on the World Energy Conference in 1963 [53]. Next, in 1969, Coca Cola company used LCA method to compare beverage containers. The methodology was evolved over the years, and standardised, namely ISO 14040, describing the principles and framework, namely the goal and scope definition as the first step of analytical procedure (ISO 14041), life cycle inventory, the life cycle impact assessment as the next two stages of analysis (ISO 14042) and the life cycle interpretation – final stage of analysis (ISO 14043). The compilation of the latter three was included into the ISO 14044 standard, which have additional aspects of analysis such as multi-functionality issues or allocation [23]. The method is very sensitive. The key, for appropriate results, is collection of all suitable data and precise definition of functional unit. The latter defines the qualitative features and quantitative aspects of the main function. It should answer basic questions such as "what?", "how much?", "how long", "where" etc. More specifically, the functional unit is reference point for scope of analysis (which unit processes should be included/excluded) [10].LCA identifies and quantifies environmental impacts of product/processes *via* impact categories. The environmental impact categories, grouping diverse emissions into the environment, are as follows: global warming, reduction of abiotic resources, eutrophication, acidification, eco-toxicity, human toxicity, ozone layer depletion, land use, photochemical oxidant formation, suspended dust and its effects on the respiratory system, ionizing radiation. These mid-points are further classified into three main damage (endpoints) categories such as eco-system quality, human health and natural resources [38,53,54].Moreover, this method enables description of "footprint". This term derives from literature: "*I was exceedingly surprised with the print of a man's naked foot on the shore, which was very plain to be seen in the sand*." [55]. It was adopted in the environmental science as "ecological footprint" by William Rees in 1992 [56]. It is an indicator helpful in monitoring human activities on natural environment. It was developed to water- [57], carbon- [58] or consumer footprint [59].We can consider either product (PCF/PEF) – or organization carbon/environmental footprints (OCF/OEF) [60–64]. Footprints measure negative environmental (and social) impacts, while new indicators known as "handprints" define positive aspects in relation to sustainable development [65].

Additional aim is preventing footprints [66–69]. Besides, the product biodiversity footprint (PBF) is a novel approach linking the LCA and ecology to support *inter alia* eco-design. Comparative assessment of the environmental impacts of products/organizations on biodiversity is considered [70].

Furthermore, Life Cycle Engineering (LCE) should be mentioned. It focuses on the development of products and processes in a life cycle perspective towards more sustainable solutions in relations to either manufacturing or consumption [71].

Bridging SDGs and LCA: a new tool helpful in realization of sustainable goals

Realization of all 17 SDGs with 169 targets, and more than 200 indicators by the 2030, is a challenge. Therefore, proper strategy and methodology which could be helpful in sustainable decisions leading to realization of ambitious sustainable goals by the end of this decade is essential and prioritised. Different tools and innovative environmental technologies are tested thanks to the initiatives of the European Commission. However, only the life cycle approach is well-suited to addressing sustainability issues/problems [39].

- The *status quo* of relations between sustainable development (and SDGs) and LCA

LCSA is the best investigated, the most important, the most suitable and complex methodology, which includes sustainability aspects from a life cycle perspective. More specifically, LCA evaluates diverse environmental impacts within entire life cycle of product, process or organization, namely from cradle to grave, or at the corresponding stages of life cycle, in various system boundaries, such as from cradle to gate, from gate to gate or from gate to grave. In the case of life cycle of products we have the following stages: extraction of raw materials, processes/production, use of the product, recycling etc. In the case of life cycle of organization, stages from building, through its performance to liquidation, are analysed. Notably, sustainability assessment should be related to the three-bottom line framework: people, ecosystem and economy. It could be linked to Life Cycle Management (LCM), including social (S-LCA), environmental (LCA) and economic (LCC) aspects of life cycle-based methodology [72]. Therefore, LCSA is the best strategy for holistic quantification and evaluation of sustainability [42]. Furthermore, other concepts related to LCA are helpful for bridging product/processes/organization-based data and the targets of SDGs. As an example, LCT, concerning eco-thinking during life cycle, is central core concept for sustainability assessment towards ambitious targets [43,73–81]. Moreover, eco-efficiency is practical dimension of sustainability. It promotes transformation of unsustainable to sustainable development. It is based on the formation of more goods/services with less environment pollution [82]. It includes economic and environmental aspects into the product improvements. This concept is helpful in the measurement of the sustainable productions and selection of best-quality eco-solutions in organisations [82]. Footprints and handprints are additional issues in the scope of LCA. Footprint approach considers the negative, while handprints [65–67] - the positive contributions of products to sustainable development. Their practicability and flexibility are helpful in solving the social (and environmental) problems included in the plan of SDGs.

- Novel LCA-SDG methodology

In view of the above, philosophy of LCSA is a base of SDGs essence. LCSA can be useful tool to measure the progress of diverse activities and products into the SDGs. Relationship between SDGs and impact category groups (health, climate etc.) is obvious. In consequence, a life cycle SDG analysis could provide data for general impact either on sustainable well-being or on each of the SDGs. Linking the SGDs with LCA indicators is promising methodology useful in analysis of companies' contributions to the SDGs ("*SDGs + LCA = impact*"). The realization of SDGs will provide additional business value (increase sustainable development of organisations resulting in additional jobs, better quality of life etc.).

The project has been started by the UN Life Cycle Initiative. It is under administration of OnePlanet, LCA Consultants and PRé-Sustainability [83]. Currently, novel proposing methodology is still tested and developed [78,84], particularly in the context of data sources, and social features, and collection as well as proper combining the impact pathways with all 17 SDGs. It should be mentioned that LCA focuses *per se* on the business and individual products, while the SDGs – on governments at global (country) level [65]. Moreover, SDGs are rather qualitative, may overlap, interact or conflict with each other [65,83,85]. On the other hand, a new methodology it seems to be flexible in relation to corresponding goals. Specific practical tests are still performed. Method should provide framework for diverse kinds of impacts evaluation in diverse contexts of applications.

At the beginning, three major stages such as development of methodology, public consultation and businesses cases were considered.

More specifically, there are two possible variants of linking LCA with SDGs: A Life Cycle SDG screening (LCSS) and methodology LCA-SDGs. The first option qualitatively combines results of LCA with SDGs. In other words, LCSS is useful in identification of potential contributions (positive and negative impacts of organisations) to the SDGs. However, the second approach considers more comprehensive holistic integration of indicators related to all SDGs. The aim is more complete and consistent qualitative analysis of corresponding impacts. It is crucial for sustainable organizations.

Basically, analytical procedure of new methodology is similar to LCA, consisting of four main steps:

- 1-definitione of goal & scope,
- 2-inventory analysis,
- 3-impact assessment,
- 4-interpretation of results.

Strictly speaking, in the first step, similar to traditional LCA, key elements, such as aim of analysis, analysed product, inputs, detailed definition of functional unit and the system boundaries, should be determined. The major questions are which SDGs, if/how/how much contribution of product to SDGs change during life cycle etc. The main sustainable aim is increasing/improving positive contribution of products to SDGs.

In the second step, collection of all suitable social and environmental data on the product system in the context of defined goal, and conversion data to a 5-point-scale of calculations are needed. The impacts (flows, inputs, outputs) on sustainable development are related with activities of people in the environmental (inputs from nature, emission to air, water, soil), economic and social dimensions (inputs from work, monetary flows, flows of unpaid goods/services). Theses human activities are quantified *via* indicators based on the SDGs (measured in the context of individual activity/organisation) [41].

The LCSA indicators can be divided into all (economic, emission and occupational indicator categories) or only specific organisations (supplying basic services, located in urban core regions, related with foods/beverages or bio-materials). In particular, these business-based inventory impact categories are as follow: economic, such as salaries, social costs, tax payments, rents etc., emission: harmful substances, radiation, noise, occupational: premature return to work, education in infective disease prevention etc. It is in progress and diverse cases are tested in practice in diverse conditions. On the other hand, majority but not all 17 SDGs can be well characterized by LCA indicators. Precise optimization of the diverse flows is still required.

In the next step of analysis, indicators as starting points and collected data of human activities are translated to impact scores related to midpoints and endpoints, which will be helpful in decision-making. The pathways of impacts as well as linking impact categories with SDGs are still ongoing.

In the final step, the results should answer the defined aim. Determination of results validity and uncertainty and data quality are needed. Life cycle SDG assessment provides quantitative results for the general impact on sustainable well-being, impact on all SDGs, their targets and indicators and for the contribution from all impact categories to mentioned earlier impacts [83].

The intention of Life Cycle-SDG-Assessment is to avoid gaps and overlaps, impact results in comparable units related to sustainable wellbeing (potential expression in monetary values) [83,85–91].

Due to multidimensional social systems, S-LCA, numerous and complex tests are necessary. Until quite recently, for the S-LCA significant differences had been observed, despite of only two indicator sets had shown only slight differences [41]. However, it gradually changes from year to year through introduction of high-quality indicators of social impacts in the context of products/processes as well as specialist databases [3,49,75,83,84]. Currently, in a capitalistic society, cities, communities, personal consumption, lifestyle of people, private households have a huge relevance in global gas emissions etc. [84]. SDGs include a more sustainable consumption. Therefore, the newest bottom-up concept – life-LCA is relevant for evaluation of whole human life and lifestyle, diverse impacts in all stages of their life, from birth to death [92]. On the other hand, it should be mentioned that Organizational Life Cycle Assessment method (O-LCA), including also social parameters, also is compiled [93,94].

Furthermore, another interesting issue is sustainability price as a new measure in relation to either social or environmental Life Cycle Costs towards a sustainable economy. It communicates the costs in relation to poverty and climate change in global supply chains. Sustainability price is the sum of the market price, additional price in terms of minimum social and environmental sustainability values [95].

To conclude, linking the impact categories with all sustainable targets and corresponding sub-targets, and selection of suitable indicators helpful in the holistic assessment of life cycle is key for new methodology. Notable progress on the development of new methodology by PRé Sustainability and 2.-0 LCA Consultants is reported [96–99]. A case studies on applicability new methodology are gradually presented, but only in selected aspects and initial insight into the results [84].

- Strengths of the LCA-SDG

The main strengths are as follow:

- it provides information on the real and potential (positive and negative) sustainability impacts, throughout entire life cycle,
- quantifies impacts in all dimensions of sustainability,

- is applicable to realization of sustainable goals, is holistic,
- integrated analytical approach in relation to corresponding sustainable targets and sub-targets,
- results support sustainable decisions via different ways,
- results can be reported in a comprehensible manner.

- Limitations

On the other hand, method also has shortcomings such as:

- huge diverse, multidimensional precise data needs,
- still relatively low maturity of S-LCA,
- uncertainties and sensitivity [42].

Impact

We summarized state-of-the art and importance of sustainable development. As pointed out at the beginning of this mini-review, sustainable development is a global priority in order to protect our planet and improvement quality of life, in relation to either current or future generations. Therefore, the establishment of the SDGs is crucial for all people all over the world. More explicitly, the paper reveals diverse methodological approaches to realization of these goals. Firstly, Life Cycle Assessment (LCA) as typical analytical tool provides information on potential impacts of products/processes/organizations on environment in either entire life cycle (from cradle to grave) or at the corresponding stages of the life cycle (e.g. from cradle to gate, from gate to gate, from gate to grave). The impacts are evaluated in three main damage categories such as human health, ecosystem quality and natural resources. More specifically, impacts can be categorized in diverse midpoint groups such as human toxicity, respiratory effects, ionizing radiation, ozone layer depletion, photochemical oxidation, aquatic ecotoxicity, terrestrial ecotoxicity, aquatic acidification, aquatic eutrophication, terrestrial acid, land occupation, global warming, non-renewable energy, mineral extraction. The next - social aspect is related with Social-Life Cycle Analysis (S-LCA), while economic - with Life Cycle Costs (LCC), including all social features and all costs during all life cycle of product, process or organization. These three concepts are described by Life Cycle Management (LCM). In addition, Life Cycle Thinking (LCT) as ecological thinking, helps to understand that all human activities have environmental impacts. It should be holistic thinking during entire life cycle and clear connection of all mentioned strategies with sustainability philosophy has been identified leading to Life Cycle Sustainable Assessment (LCSA). More analytically, every methodology has relevance and is rather complementary than competitive. In consequence, LCSA is perfect tool for realization of sustainable goals. Nevertheless, introduction of specific algorithms and parameters helpful in proper assigning potential impacts to all seventeen sustainable goals leading to correct results and interpretation, is required. In consequence, innovative methodology, called LCA-SDGs has been proposed. Added value will be not only qualitative but also quantitative holistic assessment within the entire life cycle of product or organization. The newest forms of LCA such as *inter alia* Life-LCA (LLCA), providing advanced diverse social parameters, either at the regional or at the global level, will complement studies. The results obtained from the innovative method will be valuable in making reasonable sustainable decisions. Nevertheless, it is under development. A lot of data is needed to build specialistic databases, which are compiled with the program. None of key aspects should be neglected. This work will have additional impact in popularization of new methodology, and consequently acquisition of valuable information in advanced further studies. This first, to our best knowledge, attempt to gather and analyse the knowledge in this topic is helpful, particularly as realization of SDGs is in the global priority list by the end of this decade. Moreover, we emphasize that behaviour of each of us, in daily life, has impact on quality of our planet and sustainable future of the world.

The willingness to change life, acceptance of an appropriate hierarchy of values that will shape pro-ecological attitudes in the context of life cycle thinking are key for the common good. A lifestyle changes in the context of reduction of consumption, saving, could have global benefit. To sum up, sustainable behaviour of people and the use of LCA-based concepts, and new methodology combining SDGs with LCA in a holistic way will have a great environmental, social and economic impact in effective progress to reach the global targets. Future research efforts should be directed towards incorporating as many diverse descriptors as possible, which will result in establishing quantitative criteria and construction multidisciplinary results.

This kind of review focusing on the innovative methodology, which is still under development, but extremely required in realization of sustainable goals by 2030 towards sustainable future of the world, is lacking, thus providing novelty.

Conclusions

Bad condition of our planet calls all of us to pro-ecological actions towards sustainable development of the world. Sustainable Development Global Goals should be realized to 2030, for this purpose. All seventeen goals have environmental context. Core concept could be described as "*one planet, one main goal: good life for all*". Hence, effective assessment tools helpful in sustainability concrete decisions to reach ambitious targets and sub-targets is needed. LCSA, the best known and investigated analytical complex method in relation to entire life cycle, which supports environment, economic and social dimensions of sustainable development, can be helpful in suitable identification and assessment of diverse impacts in relation to the corresponding SDGs. On the other hand, SDGs and LCA seems to be in conflict because the SDGs focuses on a macro-level (improvement of world), while LCSA - on micro level (evaluation of potential environmental impacts of particular products or organisations). SDGs were not related with business, and consequently difficult to effective measurement and results control. Nevertheless, common points were found, and linking the LCA indicators with corresponding SDGs by specialist data conversion were possible. Universal and flexible character of LCA-SDGs enables its applicability in diverse branches. Results obtained by novel LCA-SDG methodology will be helpful in sustainable decision-making, and consequently realization of ambitious global goals, including improvement quality of eco-system (and care about renewable energy), fight against unsustainable aspects in society (e.g. poverty or hunger) as well as better human well-being. The innovative LCA-SDGs methodology useful for measuring and reporting on companies' contributions to the SDGs is nearly ready, but still under development. The main disadvantage (except uncertainties as an integral part of each analysis) is the fact that a huge diverse data is required. Proposed method combines all aspects (environmental, social, economic) of sustainable development with actions of organisations. In the nearest future, continuous improvement and expansion of impact channels among indicators and SDGs are needed. Moreover, methodology focuses mainly on reduction of negative impacts of organisations. Therefore, analytical side should be expanded to additional solutions leading to obtainment of positive impacts as well. Deadline of realisation of SDGs towards sustainable global future is getting closer and closer. This mini-review as recommendation of new methodology possessing high innovation's potential to reach SGDs can leads to increase its popularity and consequently more advanced study on inventory indicators essential for proper holistic evaluation before its implementation.

Conflict of interest

There are no conflicts to declare.

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IONIC LIQUIDS AS ALTERNATIVE SOLVENTS FOR ENERGY CONSERVATION AND ENVIRONMENTAL ENGINEERING

Sachind Prabha Padinhattath
Department of Chemistry, Indian Institute of Technology Madras
Chennai 600 036, India, sachindprabha@gmail.com

Baiju Chenthamara
Department of Chemistry, Indian Institute of Technology Madras
Chennai 600 036, India, baijucsiitm@gmail.com

Ramesh L. Gardas*
Department of Chemistry, Indian Institute of Technology Madras
Chennai 600 036, India, gardas@iitm.ac.in

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Abstract

Because of industrialization and modernization, phenomenal changes have taken place in almost all spheres of life. Consequently, the consumption of energy resources and the cases of environmental hazards have risen to an unprecedentedly high level. A development model with due consideration to nature and an efficient utilization of energy sources has become the need of the hour, in order to ensure a sustainable balance between the environmental and technological needs. Recent studies have identified the suitability of ionic liquids (ILs), often labeled as 'green solvents', in the efficient utilization of energy resources and activities such as bio-extraction, pollution control, CO_2 capture, waste management etc. in an environmentally friendly manner. The advent of magnetic ionic liquids (MILs) and deep eutectic solvents (DESs) have opened possibilities for a circular economic approach in this filed. This review intends to analyze the environmental and energy wise consumption of a wide variety of ionic liquids and their potential towards future.

Key words

Ionic liquid, green solvent, energy resources, pollution control, bio-extraction, circular economic approach

Introduction

Development is the need of the hour, but proper planning and wise use of resources should be vital in minimizing the side effects and achieving the desired targets. The twenty-first-century witnesses a peak in the efforts to establish methodologies, technical support and socio-economic studies related to developmental activities [1]. The attempts to achieve the development envisioned inevitably results in the pollution of the environment. Non-sustainable utilization of energy resources has also aggravated the exploitation of nature and instances of pollution [2]. There is in fact a popular saying that 'any development which lacks its concern on nature is as good as being suicidal'. Even in recent times, our society is confronted by the detrimental impacts of industrialization and modernization which were preceded by globalization policies. Despite all the developments that we have achieved, we still struggle with unaddressed issues such as global warming, acid rains, air pollution, improper waste management and so forth. Therefore, one needs to note here that the method of development, efficient utilization of the energy resources and conservation of nature are interlinked to each other. An eco-friendly sustainable development model that maintains a holistic balance between these three aspects has undoubtedly become a necessity [3].

It is in this context the emergence of a new class of chemicals, namely ionic liquids (ILs), become vital [4]. Room temperature ionic liquids (RTILs) are a class of non-molecular compounds that are comprised of only ions with advantages in various physicochemical properties such as negligible vapor pressure, high thermal stability, high extraction capability, and tunability according to applications. Owing to these unique characteristics, ILs have the prospects to be a tool to achieve sustainable development and are often referred to as "green solvents". Due to their unique properties in comparison to conventional chemicals, RTILs have been extensively used in various fields including metal processing, bio-catalysis, environmental remediation and biological extractions [5–7]. New generation ionic liquids, which are a version of the above mentioned, incorporate transition metal or rare-earth metal ions in their structure and possess inherent magnetic properties. These ILs were categorized as magnetic ionic liquids (MILs) and have got advantages over conventional RTILs in thermal stability, vapor pressure,

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magnetic separation and recycling [8,9]. Similarly, as they share multiple properties and characteristics with ILs, deep eutectic solvents (DESs) are now commonly accepted as a new class of ionic liquid analogues. DESs are systems formed by a eutectic combination of Lewis or Bronsted acids and bases which could contain a number of anionic and cationic species. [10]. All these chemicals are categorized under 'ionic liquid chemistry'- the most explored branch of chemistry in recent years. The major increase in the number of publications in this field year by year indicates the importance and wide use of ILs in key areas (Fig. 1).

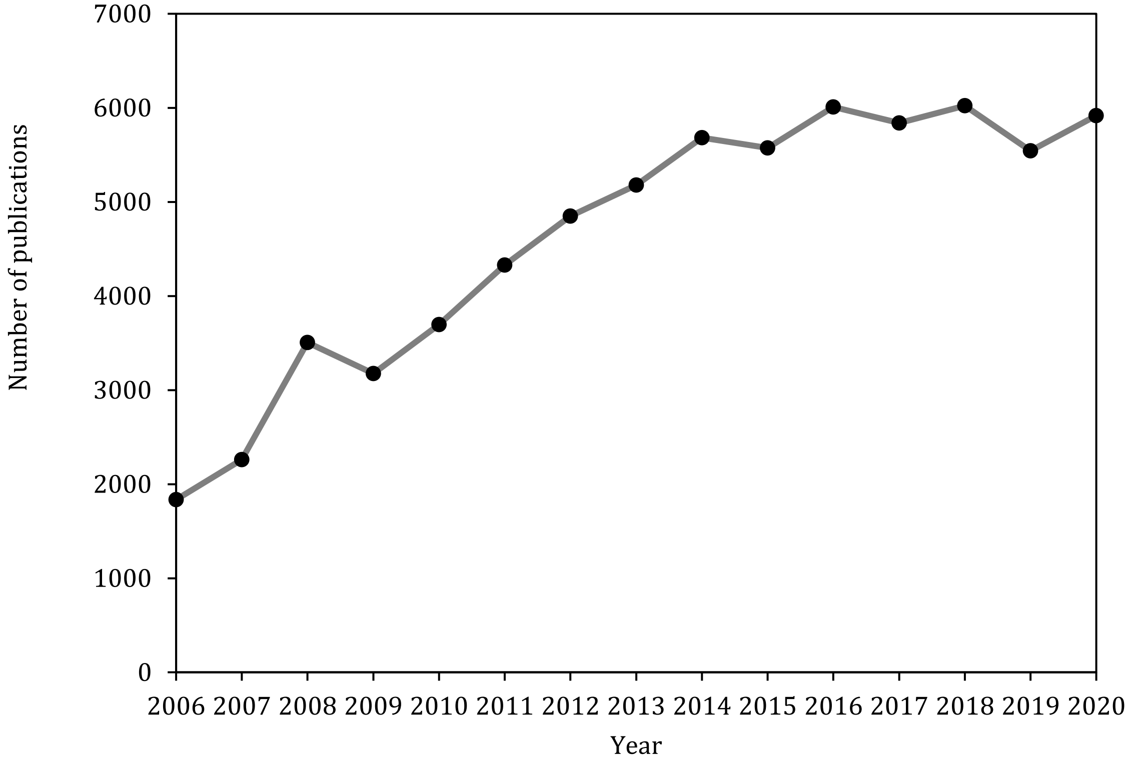

Fig. 1. Year wise publications on ionic liquids from 2006 to 2020. *Source: SCOPUS*

The current review addresses the environmental concerns and inefficient energy resource utilization and analyzes the role of ionic liquid chemistry to tackle these hurdles. Conventionally, organic solvents have been extensively utilized for these applications. They are highly volatile, cytotoxic as well as ecotoxic. These disadvantages can be rectified by the use task-specific ionic liquids, as we can design them according to the desired application. As the area of interest is very vast, the main focal points were restricted to the role of ILs in crude oil industry, refrigeration process, CO_2 sequestration and wastewater management. This study also attempts to brief the application of ILs in the extraction and storage of biomolecules, which could unveil their importance as a bio-economic tool. The recent research trend in these fields is depicted (Fig. 2) and the constant increase in the number of publications towards this end indicates the unavoidable role of IL chemistry in our area of interest. Therefore, a deeper analysis of these results and a detailed study of the ionic liquids involved in them will obviously help to sharpen and reemphasize the goals of sustainable development. This can further help to improve the developmental efforts in the above-mentioned fields, as envisioned in this review.

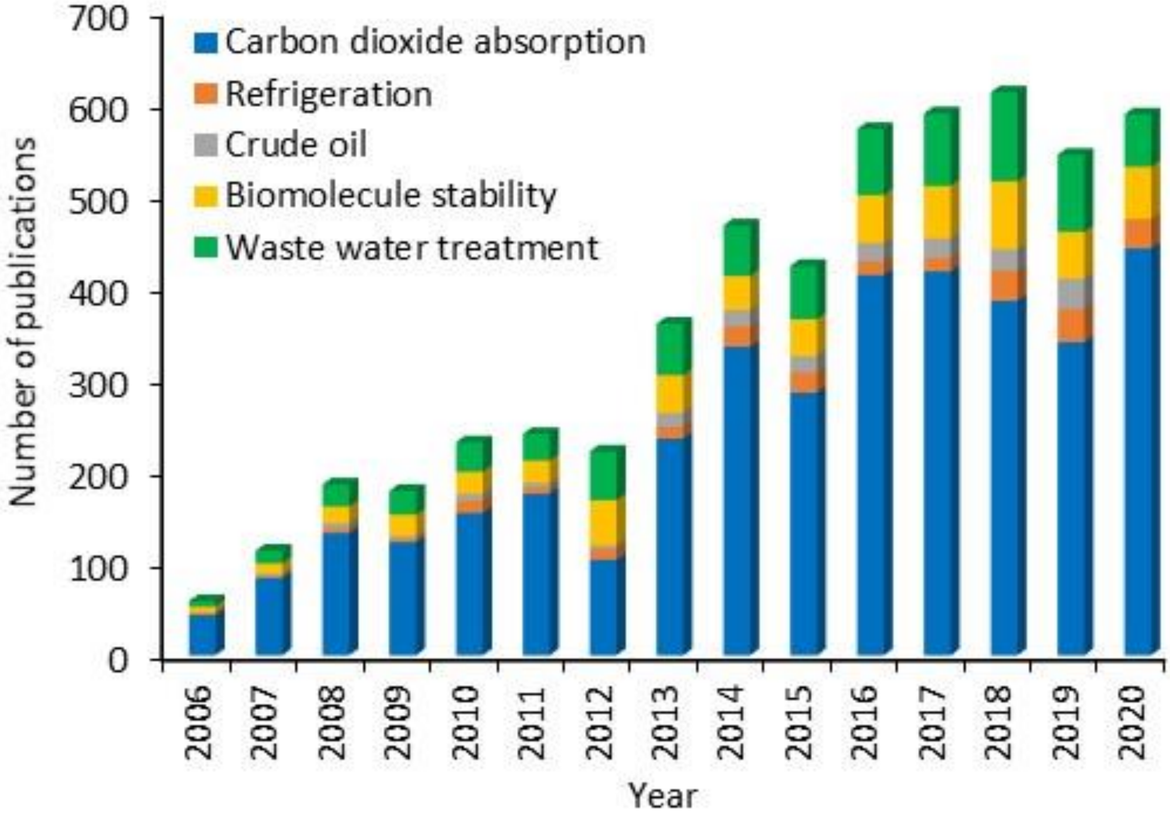

Fig. 2. Recent research trend in ionic liquids for the field of energy and environmental engineering. *Source: SCOPUS*

Role of green solvents in sustainable development

As mentioned in the introduction part, the role of ionic liquids and deep eutectic solvents in energy conservation and in environmental engineering is being discussed in detail under four subtopics.

Crude Oil Industry

The oil and gas industry forms the lifeblood of the global market and is one of the major contributors to the global economy. The economic framework of any nation is greatly influenced by the detection of oil fields, processing and production of oil. The dominance of oil as a potential energy source is attributed to its indispensability in the transport sector and the production of many everyday essentials. The refined products developed from oil constitute the key ingredients for the manufacture of almost all chemical products and other commercial goods [11]. The oil and gas industry can be broadly broken down into three segments based on their operational responsibilities: upstream, midstream and downstream. The primary responsibilities of upstream companies include exploration of reservoirs and drilling of oil and gas wells. Midstream and downstream companies are responsible for shipping crude oil from wells to refineries, refining and distributing oil products. Upstream oil industry can be classified into four categories: drilling operations, enhanced recovery of oil, non-conventional heavy oil recovery and flow assurance. The extreme conditions associated with these operations, such as high reservoir salinity, high temperature and heat, render the use of normal solvents undesirable. Because of their unique chemical characteristics, especially the ease of tunability, ionic liquids have therefore emerged as a suitable alternative. Ionic liquids can function as an extraction agent during downstream refining processes to eliminate impurities from crude oil derivatives [12,13].

A fluid or mixtures of fluids, namely drilling fluid, is typically used in operations that involve the drilling of a borehole into the earth. According to the composition, these drilling fluids can be classified as water-based, non-aqueous based and pneumatic. A critical challenge in drilling applications is the development of cake buildup, resulting from the leakage of the drilling fluid into the formation matrix. Although cake build up to a certain degree is desirable, the excess formation of the same can result in stuck pipe issue and other drilling problems. Fluid-loss additives are generally used to control this process and avoid potential reservoir damage [14]. Recent literature studies show that ionic liquids can be used prospectively to control this fluid loss. A study on the feasibility of the use of ionic liquids as a potential drilling fluid additive for high-temperature wells has been envisaged by Ofei et al. [15]. The study validates the use of ionic liquids as a drilling fluid additive and their capability to maintain the rheological properties of water-based mud at high operating temperatures. The rheological and filtration behaviors of water-based drilling mud have been studied by using 1-butyl-3-methylimidazoliumchloride (BMIM-Cl) as the model compound, over a temperature ranging from room temperature to 200 °C and to a pressure limit of 1000 PSI. The study indicates that the addition of BMIM-Cl stabilized the viscosity of the mud, solid suspension capacity and filtration behaviors up to 180 ° C. Further, the suitability of 1-methyl-3-octylimidazolium tetrafluoroborate (OMIM-BF_4) was evaluated as a possible additive to polymer-water based mud [16]. The results from this study reveal that OMIM-BF_4 has effectively improved the rheological properties as well as the consistency index of the polymer-water based mud. The key factor which attributes to this improved behavior is the presence of long alkyl chain in OMIM-BF_4 and thereby the possibility of hydrophobic adsorption. Another example of the fact related to drilling fluid additives has been established by Yang et al. Their main focus was on bentonite/water-based drilling fluids, which were characterized by a significant fluid loss due to high temperature-pressure levels and divalent cation concentrations. The filtration control was achieved through free radical copolymerization in presence of 1-vinyl-3-ethylimidazolium bromide [17]. The in-depth studies on the rheological and hydration inhibition potentials have provided systematic guidelines to design novel sets of drilling fluid- IL combinations for the drilling of gas hydrate rocks [18–20].

In addition, ILs and DES have also been used as clay stabilizers and shale hydration inhibiters. Clay swelling is a type of damage that results in the reduction of formation permeability due to the alteration of clay equilibrium. The influx of water-based filter fluids into the forming matrix and ion exchange are two major factors for the occurrence of the clay swelling. To solve this issue, it is very important to understand the structure of the clay and its chemical condition at the moment of contact. Chemical additives (clay stabilizers) may be used as a measure to reduce clay swelling. The filtrate fluid's charge and electrolytic properties can be efficiently controlled by the clay stabilizers and the clay platelets can be held in place. Imidazolium-based ionic liquids have been identified as a possible inhibitor of clay swelling and research in this area is progressing at a brisk pace [21]. Shale oil is the unconventional oil extracted from a class of fine-grained classic sedimentary rocks known as shale rocks. Shale hydration results from the interaction between the exposed shale formation and water-based drilling fluids during reservoir exploration. Therefore, the research on shale hydration inhibitor is worthwhile. Luo et al. initiated the studies on the potential of ionic liquid as shale hydration inhibitor. They have prepared a model drilling fuel by mixing distilled water, sodium montmorillonite and sodium carbonate. Through various tests, they have proved the greater affinity of the drilling fluid towards the inhibitor ionic liquid 1-octyl-3-methylimidazolium tetrafluoroborate [22]. Yang et al. synthesized 1-vinyl-3-ethylimidazolium bromide and analyzed its performance as a shale hydration inhibitor in detail [23]. Later, the effect of alkyl-chain lengths on the vinylimidazolium group on hydration inhibition activity was analyzed by the same group. The efficiency of IL inhibition decreased with increase in alkyl-chain length. When alkyl chain length increases, IL molecular volume increases while the hydrophilicity and solubility of the IL decreases. This minimizes the interlayer space and thereby the hydration inhibition activity. [24]. The effect of 1-octyl-3-methylimidazolium bromide (OMB) as shale hydration inhibition agent has been explored by Xu et al. Compared to conventional shale inhibitors, superior shale hydration inhibition properties were observed in the case of OMB. [25].

Ionic liquids have an undisputed role in the enhanced oil recovery (EOR). Enhanced oil recovery (improved oil recovery), which generally happens in the third stage of oil recovery, restores formation pressure and improves oil displacement in the reservoir. The oil recovery enhancement method using sophisticated techniques alters the original properties of the oil. Ionic liquids can alter the wettability and interfacial tension accordingly to the required levels and are stable under high temperature and high saline conditions within the reservoir [26]. Therefore, ILs were identified as the right candidates EOR processes. In a detailed review on surface-active ionic liquids used in surfactant-based enhanced oil recovery processes, Nandwani et al. analyzed recent trends in this particular field. Their review focuses on the efficiency of surface-active ionic liquids (SAILs) to reduce interfacial tension (IFT) between oil and water under prohibitive environmental conditions. The study compares different SAILs used in EOR applications till date and lists out their advantages and disadvantages [27]. Prathibha et al. studied the advantages of polyionic liquids (PILs) in the field of EOR. Their primary focus was on the EOR properties of poly [1-hexadecyl-3-vinyl-imidazolium bromide]. The study analyzed the interaction of the synthesized PIL with aqueous injection fluids and crude oil with respect to different properties such as interfacial tension, wettability alteration and dynamic light scattering (DLS). IFT values were decreased with increase in temperature and salinity. The importance of poly ionic liquids in the EOR process is underscored by the positive observations obtained during the wettability and DLS studies [28,29].

Unconventional heavy oil recovery field has also started utilizing the services of ionic liquid chemistry in recent times. Unconventional recovery is the recovery of oil other than conventional method. This unconventionality can occur in resource characteristics, production technologies, economic environment or the scale of production.

Coal bed methane, gas hydrates, shale gas, fractured reservoirs and tight gas sands are considered as unconventional resources. The major application of ionic liquids in this field is that they could act as a viscosity reduction agent of heavy crude and as an effective kerogen extractant (kerogen is the portion of naturally occurring organic matter that is non-extractable using typical organic solvents) [30]. Flow assurance, which involves design, techniques and principles for ensuring uninterrupted hydrocarbon supply from the reservoir to the point of sale, is another crucial task in the crude oil industry. As they move into the processing plant, fluids undergo changes in pressure and temperature and result in multiple fluid phases. In consequence, the formation, accumulation and dispersal of inorganic and organic solids can occur. Major disadvantages of this process are asphaltene precipitation, wax deposition and gas hydrate formation. According to recent studies, ionic liquids have the capacity to control asphaltene precipitation, wax deposition and they act as methane gas hydrate inhibitors [31].

Processing of crude oil is essential from economic and environmental perspectives. Contemporary research shows that dispersion of crude oil, oil acidity reduction, bitumen extraction, carbonate mineral separation and many other related processes can be carried out using ionic liquids [32–35]. Removal of hazardous particles has greater significance because it will increase the efficiency of the fuel as well as decrease harmful emissions during burning. For example, air pollution and even acid rain is caused by the emission of toxic sulfur and nitrogen oxides during fuel combustion. Therefore, its removal from the fuel is significant. Recently, ionic liquids have been developed to extract sulfur and nitrogen compounds from petroleum and fuels. Ionic liquids are used to extract S- and N- compounds either combined or selective. ILs were found to be far better option than classical desulfurization and denitrogenation agents due to their enhanced efficiency and selectivity [36]. Wang et al. have examined over the ability of oxidative desulphurization of coal, as the sulfur dioxide and soot which emerges out during the combustion of coal are the main sources of air pollution. In their investigation, they have used imidazolium based ILs, namely, 1-butyl-3-methylimidazolium bisulfate and 1-carboxymethyl-3-methylimidazolium bisulfate to extract sulfur from coal [37] Patra et al. analyzed the effect of nitro groups on desulfurization efficiency of benzyl substituted imidazolium-based ionic liquids. The liquid-liquid microextraction approach was adopted and the parameters influencing extraction efficiency, such as the effect of IL volume, concentration and rotation period, were extensively studied. The analysis focused on the effect of Lewis acidity, the availability of the Lewis acid site and the π-π interaction on the efficiency of desulphurization of ILs. [38]. However, its main disadvantage lies in the sessions of regeneration and recycling. The limitations of ILs such as environmental biodegradation, bioaccumulation and corrosivity have to be addressed and the researchers have to focus on the ways to overcome it.

Majority of studies on the application of ionic liquids in the crude oil industry are based on microscale laboratory experiments. Therefore, recommending them instead of conventional chemicals for the field application has to be done after extensive large-scale testing. However, the growth and development of ionic liquid in this domain is remarkable. Recent article on the role of ionic liquid catalysts in trans-esterification of different feedstock oils to biodiesel [39] is opening up a possibility of an eco-friendly economy. Scientists are even experimenting with ionic liquids to develop it as an alternate fuel by modifying the chemical structure. Though it is too early to predict the effectiveness of ionic liquids in large scale crude oil production, laboratory experiments are offering hope towards an eco-friendly sustainable development.

Refrigeration systems

Refrigeration is the process of cooling a space or a substance below room temperature, which indeed is an energy consuming process. Compression and absorption refrigeration systems are the two most common refrigeration systems used for household and industrial applications [40]. In compression cycles, gaseous refrigerant is compressed at low temperature and pressure in the compression chamber and is entered to the throttling valve. Here it expands and releases the pressure, consequent to which the temperature of the surrounding drops down. Whereas, in the case of absorption refrigeration systems, a liquid refrigerant gets evaporated at low partial pressure with the help of renewable heat energy sources or waste heat, drawing away some amount of heat with it giving rise to a cooling effect. Later, this refrigerant in gaseous form is absorbed by another fluid from refrigerant- saturated liquid solution having low partial pressure. The refrigerant-saturated liquid is then heated, causing the evaporation of refrigerant [41].

Hydrofluorocarbon (HFCs) and hydrofluoroolefins (HFOs) have been proposed as the new generation refrigerant in refrigeration and cryogenic process, which creates low temperature spaces, nearly cryogenic temperature range (-150 ˚C to -273 ˚C). However, they cause a lot of environmental problems like global warming and ozone layer depletion [42]. Therefore, the research on designing more efficient and environment friendly refrigerants and refrigerant/absorbent pairs with improved cooling capacity and coefficient of performance (COP) is essential. Considering the properties of the refrigerant, it should have high enthalpy of vaporization, low molar mass and high solubility in the selected absorbent to minimize the operating and investment costs [43]. The coefficient of performance (COP) of the refrigerator depends on the solubility of refrigerant in corresponding absorbents. The absorbent must be a fluid with a low vapor pressure to avert its evaporation. In addition, it should possess a low freezing temperature. Low viscosity of absorbent reduces the energy spent during transport and improves flux of mass and energy [44]. Finally, it is essential that both refrigerants and absorbents should be thermally and chemically stable over a range of temperatures.

Water, though non-toxic and non-flammable and shows high enthalpy of vaporization per unit mass, is not a well preferred choice as a refrigerant at temperatures below 0 ˚C and atmosphere pressure, owing to its high triple point temperature and low vapor pressure [43]. Use of H_2O with LiBr as absorbent in absorption refrigeration cycle is an example of a conventional refrigerant/absorbent pair, showing high performance due to their high solubility and the high-water mass cooling capacity. The major disadvantage of H_2O-LiBr systems is the crystallization of absorbent rich solution at low temperatures [45]. Alternatively, NH_3/H_2O system can work as a refrigerant/absorbent pair at temperature -77 ˚C and pressures near 4-20 bar. The limitation of this mixture is the small difference in volatility between the compounds [46].

Recent studies have explored the use of Ionic liquids (ILs) as an alternative to the traditional absorbents, by virtue of their high absorption capacity of gases, very low vapor pressure and good thermal stability. Low volatility of ILs allows the separation of refrigerant in refrigerant/ absorbent mixture [47]. Solubility of NH_3 on imidazolium ILs with different chain length have been studied by Li et al. and is concluded that NH_3 solubility increases with increase in cation chain length [48]. In order to improve the solubility of ammonia in ILs, Bai et al. proposed a new idea of introducing Na^+ ions into ILs for the first time [49]. Since the refrigeration experiments are more expensive and sometimes dangerous, theoretical approaches have also been envisaged to correlate the gas solubility in various ionic liquids. Karakatsani et al. used the tPCPSAFT association model [50] to tackle the task while Shiflett and Yokozeki used the Redlich-Kwong EoS model for the same. Later studies by Yokozeki et al. approached the task through a generic van der Waals EoS [51] while Freitas et al. used two cubic equations of state (PR and SRK) with van der Waals 2-parameter mixing [52] rules (vdW-2) to test the theoretical probabilities. The more promising approach in this field was carried out by Shojaeian et al., where they have used Peng Robinson-two State equation of state in order to correlate the gas solubility in various ionic liquids [53]. Moreno et al. studied different combinations of refrigerant/IL pairs out of 8 refrigerants in 900 ionic liquids using Henry's constant as the key thermodynamic parameter and COSMO-RS molecular simulations [40]. All theoretical models mentioned above, successfully predicted the solubility of refrigerant gases in ILs in the absorption cycle for different cooling temperatures.

Apart from this, ILs have been proposed as mass separating agent called entrainer for the separation of azeotropic or close-boiling point blends of refrigerant gases (HFCs and HFOs) and provide selective solubility [42]. HFCs solubility in different ILs is associated with their ability to form hydrogen bonds and different HFC compounds show different solubility due to their differences in molecular masses [54]. Delgado et al. studied the selectivity of [C_2mim] [SCN], on the separation of HFCs and HFOs, due to its low molar mass and low viscosity [55]. Shiflett et al. have correlated the solubility behavior of refrigerants with the electric dipole moment and have inferred that more the value of dipole moment, higher is the solubility [47]. Morais et al. studied the vapor-liquid equilibrium (VLE) of HFC-32 and HFC-125 in fluorinated and non-fluorinated imidazolium based ILs and HFC compounds have shown more affinity towards fluorinated ILs [55]. Delgado et al. studied solubility and diffusivity of HFC-32, HFC-134a, and HFO-1234yf in less viscous ILs and concluded that solvation is enthalpically favorable and entropically unfavorable [56].

In nutshell, to date, the major studies on the role of ILs in refrigerant chemistry is analyzed from a theoretical perspective. Once the theoretical data looks convincing, scientists can proceed to the micro-scale laboratory level and then to a large-scale industrial level. The hopeful fact is that some of the research groups have preceded to the second stage which focuses on the practical applicability of the developed refrigerant/absorbent combination based on ILs to wet lab conditions. In addition, studies have also been carried out to develop ionic liquids that can be operated in cryogenic conditions without losing the fluid properties. Another developing area of research is towards developing ionic liquids with improved ammonia solubility, which can be prospective substitute for HFC based refrigerants used in household applications.

Environmental Applications
The whole world is striving to achieve the ultimate development in each sector, but unfortunately, it is happening at the expense of environment. It is imperative to reduce the number of processes that are hazardous to the nature, but the fact is that most of these processes are the bedrock of the global economy. This contradiction is the main point to address, especially in the current circumstances. This is where the concept of eco-friendly sustainable development comes into the picture. Proper treatment of industrial effluent, controlling the smoke from vehicles and industries, waste management, reducing biomagnifications and a multitude of such herculean tasks are out there in front of the human community. Latest studies illustrate that ionic liquids have the potential to address some of these environmental issues and some are capable of pollution control. The numerous structural modifications possible on the anionic and cationic moieties in ILs allow us to synthesize compounds with desired characteristics. These special properties of ILs have the benefit in the environmental engineering as we can design a particular ionic liquid to address a particular environmental issue.

Greenhouse gas emission, especially from natural gas sweetening and flue gas treatment, causes global warming. CO_2 is a well-known greenhouse gas that contributes significantly to climate change and global warming. A report published in 2018 by the Intergovernmental Panel on Climate Change (IPCC) titled "Global Warming of 1.5" states that global temperatures are expected to rise by 1.5˚C in 2030 [57]. To minimize global warming and ocean acidification, it is very important to control the excessive concentration of CO_2 in the atmosphere. Several techniques such as absorption, adsorption, membrane separation and bio fixation have been developed in this field. But they are inadequate in terms of efficiency. Therefore, researchers in this area have been motivated to develop efficient, cost-effective and novel materials for capturing greenhouse gases and ionic liquids are at the forefront of contemporary research in this field. Blanchard et al. reported that CO_2 is highly soluble in 1-butyl-3-methyl imidazolium hexafluroborate ([BMIM][BF_6]) [58]. Later studies were conducted to improve the solubility range of CO_2 in ILs. The solubility of CO_2 seemed to be increased by amino-functionalized task-specific ILs with imidazole or pyridine ring. Based on the interaction of the CO_2-amine group, ILs containing multiple amine sites were developed [59]. A new dual functionalized IL containing amine and amino acid groups in the imidazolium ring was prepared by Lu et al. High CO_2 absorption capability, thermal tolerance and regeneration capacity were exhibited by these ILs [60]. Recently, Martin et.al proposed a study on selection and characterization of non-ideal ionic liquids in CO_2 capture [61]. A novel absorbent medium comprised of amino-functionalized ionic liquids (AFILs) dissolved in ethanol-water solvent was developed by Huang et al. The solution gets separated into two phases after CO_2 absorption and this phase transition behavior depends on the water-ethanol ratio [59]. In addition to the effect of functional group, the nature of cations and anions plays a key role in the capture of CO_2. Aki et al. reported that with the increase in alkyl chain length from butyl to octyl, CO_2 solubility is getting increased [62]. A series of amine-functionalized imidazolium cation-based ionic liquids with different anions were studied by Sharma et al. and found that anions containing fluorine had a stronger affinity for CO_2 capture [63]. Ramkumar et.al conducted the studies on CO_2 absorption capacity of guanidinium based carboxylate ionic liquids and found to be highly efficient [64]. Another method that is extensively used for the selective isolation of CO_2 is membrane separation. A membrane technology called supporting ionic liquid membrane (SILM), is used in this technique to achieve gas separation. Poly-ILs were observed to have greater absorption capacities and faster rates of absorption/desorption rate than monomers of ILs, and can thus be considered as very promising candidates for membrane material [65]. The suitability of deep eutectic solvents (DESs) as a possible solution to ILs has also been explored in recent studies. This has many favorable benefits compared to normal ILs, such as biocompatibility, biodegradability and recyclability. The primary drawback of ILs and DES is their high viscosity. Ren et al. synthesized DES based on hydrophilic polyols such as L-arginine and glycerol for CO_2 solubility to address this issue [66].

The significance of ionic liquid in wastewater treatment is another field that has been extensively studied. The dispersive liquid-liquid extraction method is used to perform most of these studies [67]. As they are directly discharged to the river or any other aquatic reservoirs, improper treatment of industrial effluents may cause a plethora of problems. This can have a negative impact on the life cycle of marine animals and can alter the equilibrium of the existing ecosystem. The removal of heavy metal from activated sludge and wastewater is of prime importance since many terrible incidents have already happened in our world, such as the Minamata incident. Removal techniques for heavy metals like cadmium and lead from drainage samples and activated sewage using quaternary ammonium and phosphonium ILs were demonstrated by Fuerhacker et al. in 2012 [68]. Heavy metal removal from activated sludge has proven to be more efficient than conventional approaches such as incineration and extraction by acid. Proper and scientific management of textile wastewater containing colorants and other chemicals is of great importance. With the use of activated carbon modified ionic liquid, Afrin et al. have put forward an innovative approach for handling wastewater from the textile industry [69].

In contrast with traditional methodologies, this approach yielded good results and demonstrated advantages in terms of selectivity, stability and adsorption capability. According to Tangatova et al. certain ionic liquids can influence microorganisms present in the activated sludge and accelerate the rate of biological wastewater treatment [70]. The removal of various forms of organic contaminants such as pesticides, insecticides, micro-pollutants and other chemical components from the water resources is a sub-area of the same field, and the advancement of research in this area is also worth noting. Jingying et al. have conducted studies on the separation, recycling and management of a large variety of organic contaminants with ILs. Phenolic agents, toxins, solid waste and some waste gases were in this list of pollutants [71].

With the introduction of magnetic ionic liquids and deep eutectic solvents, research related to wastewater treatment has been elevated to the next level. A wide range of MILs and DESs have been synthesized for the extraction of pollutants. Hydrophobicity, structure and Lewis acidity of MILs/DESs play a key role in the extraction efficiency. Their significant advantages are recyclability and reusability. Florindo et al. have put forward a circular method using hydrophobic deep eutectic solvents to purify water polluted with micro-pollutant drugs. Ciprofloxacin, classified as one of the top ten important micropollutants, has been isolated using DESs comprising quaternary ammonium salts and natural fatty acids. A circular method has been developed by the group to recycle and reuse hydrophobic DES through the use of activated carbon [72]. Sas et al. focused on the elimination of phenolic pollutants from water reservoirs using organic acids and DESs based on menthol. The findings obtained from similar RTILs were compared with the experimental data and was shown to be more advanced [73]. Silva et al. employed magnetic ionic liquids to identify organic pollutants in river water samples [74]. The detection and elimination of pesticides from water sources is also of primary importance. Since the advent of ionic liquid chemistry, research in this field has found a new vigor. Liu et.al, conducted a series of experiments to detect, extract and analyze organophsophorous pesticides from water samples with imidazolium ionic liquid and the findings were promising [75]. A similar method was explored by Tatjana et al. in which the imidazolium ionic liquid-based vortex-assisted liquid-liquid microextraction method was used to determine the presence of four pesticides in an industrial wastewater sample [76]. Wilms et al. recently performed a detailed study on the potentials and possibilities of herbicidal ionic liquids. This study objectively analyzes both the merits and demerits of ionic liquids in the view of herbicidal properties and adds their thoughts to improve the contemporary research methodologies [77].

Modern research studies concentrate on the development of new ionic liquids that are more eco-friendly and efficient for the extraction of contaminants [78]. For the aforementioned reason, efforts have also been made to design biocompatible polymeric ILs. In addition, experiments based on magnetic ionic liquids are proceeding in the right direction, and this can deliver a groundbreaking result in terms of reusability. Recently researchers are also showing interest in the designing of IL-coated membranes that are biocompatible for the same application. Scientists are also in pursuit of developing methods for regenerating the absorbed CO_2 in order to produce fuel out of it which is a big hope in the field of renewable energy and engineering.

Biomolecule extraction

Production, extraction, purification and storage of bioactive compounds are getting much attention in modern day research because of their unavoidable role as a biochemical and nanotechnological tool. The existing methods to extract and purify biomolecules incorporate environmentally hazardous chemicals and have several other drawbacks such as low extraction efficiencies, poor selectivity and lack of cost effectiveness. Most of the existing methodologies require multiple and nonconventional operations which could affect the molecule's inherent biological nature and properties. To rectify these disadvantages, scientists were in active quest for an alternative solvent, and it resulted in the incorporation of ionic liquid in the field of biomass extraction. Applications of ionic liquids in the biological and biomedical field are getting explored rapidly in recent times as they possess improved solvation ability, easily tunable nature and environmental benign behavior. They are task specific solvents, the quality which improves the extraction efficiency and relaxes the hectic purification procedures. To analyze the growth in this area of research a wide range of bioactive compounds can be considered, but our area of focus is restricted to the field of amino acids, proteins and nucleic acid chemistry where the ionic liquid related research is at top gear. [79–82]

Proteins are macromolecules of structural units called amino acids *and they* are very much essential in the vital functioning of an organism. In addition, proteins have got huge impact in different industrial sectors. The isolation and storage of proteins are, therefore, very important in biological and economic sense. The ability of ILs to enhance the stability of the native states of proteins, to gear up their refolding capacity and to subdue the irreversible aggregation pattern have provided a new outlook to the protein related research. Amino acid extraction and storage is also very much essential as they are the building blocks of any protein. According to the literature, there are four main techniques used in amino acid and protein extraction namely solid phase extraction (SPE), liquid-liquid extraction (LLE), IL-based three-phase partitioning (TPP) and IL-based aqueous biphasic systems (ABS) [79].

IL-based SPE methods aimed at extracting amino acids and proteins was mainly done through IL modified materials – such as IL immobilized silica and ILs on the molecularly imprinted polymers (MIPs). Direct extraction technique was also attempted by various groups of scientists, but in general, SLE is less explored due to the relative difficulty to establish the experimental setup and lower extraction efficiency. Liquid-liquid extraction emerged as an effective substitute due to its advantages in experimental pattern, selectivity and extraction efficiency. The pioneering study in the amino acid extractions based on LLE approach was done in 2003 where 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6) as the extractant. Tryptophan, glycine, alanine and leucine were amongst the amino acids and some of them were not directly soluble in this ionic liquid. To have similar extraction efficiencies for both hydrophilic and hydrophobic amino acids, the ionic liquid structure was modified by adding the crown ether [dibenzo-18-crown-6] at acidic pH [80]. Following this, Smirnova et.al attempted the extraction of a wide variety of amino acids by using the same ionic liquid. The extraction was from aqueous solution to the IL phase with dicyclohexano-18-crown-6 as an additive (pH range 1.5- 5.5). The most hydrophilic amino acids were extracted as efficiently as the less hydrophilic and the extraction efficiency was above 90 percent. The influence of pH, amino acid and crown ether concentration and volume ratio in this process were studied in depth [81]. The synthesis of hydrophobic ILs by tuning the cationic and anionic moieties was achieved later in the decade since hydrophobicity was the key property which influenced the flow of majority of amino acids to the IL rich medium. Imidazolium based long chain ILs were widely used for this application [82–84]. Back extraction was done mainly by specific buffers. In Parallel, the efforts to extract a wide variety of proteins were also flourishing. But the scope of the studies was restricted by the fact that the dissolution of protein required the presence of hydrated ionic liquids. Still, many proteins including lysozyme, cytochrome-c and heme were extracted successfully by LLE method [85].

The biggest drawback of LLE lies in the use of organic solvents, which may have a detrimental effect on biomolecules, human health and the environment. As an alternative to conventional extraction methods, aqueous biphasic system (ABS) has been researched due to the aforementioned reasons. Aqueous biphasic systems (ABS) are also a class of liquid-liquid extraction systems which, due to their potential use as alternatives for organic solvents in extraction and separation systems, have gained considerable interest in the research community. The main benefit of using ABS is that it is composed of two water-soluble solutes that separate into two co-existing phases at their optimum concentration. Since the major constituent is water, ABS is more biocompatible and also provides benign media for the extraction of various biomolecules. Here the extraction takes place based on the various interaction between extractant and biomolecules such as hydrogen bonding, π-interactions, electrostatic interaction and hydrophobic interactions by which biomolecules get separated to either IL rich phase or salt-rich phase. The studies on amino acid extraction with IL based ABS by Ventura et al. is worth mentioning. In their work, a wide range of imidazolium- based ILs were studied in detail. The extraction capacity of the ABS was evaluated through the extraction of amino acid L-tryptophan. Extraction capability was analyzed by setting different kind of cation anion combinations. As the hydrogen bond acidity of the IL anion plays a crucial role in the formation of ABS, the anion effect on ABS formation was found to be pivotal [86]. The amino acid extraction efficiency of ABS in the presence of biodegradable organic salt has been studied by Ferreira et al. The organic salt potassium citrate was conjugated with imidazolium-, pyrrolidinium-, phosphonium- and ammonium based ILs for L-typtophan extraction. The study underlined the fact that hydrophobic interaction has a major role to play in the whole process. They also observed that the separation of biomolecules between the ABS phases depends on their affinity for each other, which further depends on parameters such as pH, temperature and composition of the system. [87]. Following this many groups investigated the amino acid extraction through ABS technique. An interesting one to mention is by Priyanka et al. In the presence of different potassium salts at 298.15 K, they analyzed the phase activity of benzyltrimethylammonium chloride and benzyltributylammonium chloride. The effect of substitution of the benzyl group on the IL cation and the nature of different potassium salts on the phase activity were studied. In the presence of different potassium salts, these IL-based ABS have been systematically scrutinized for their efficacy in tryptophan extraction. For the examined combinations of ILs and inorganic salts, improved extraction coefficients were achieved [88]. Many studies on IL based ABS for protein extraction were also reported. Since protein is a larger moiety in comparison with amino acid, the factors influencing the stability of proteins in IL medium was analyzed in prior. It is found that the selection of constituent ions and the chemical nature of the ILs play a critical role in the stability. ILs containing high kosmotropic anions and cations with enhanced chaotropicity showed a higher efficiency. The observations made by Du et al. is of prime importance. To directly isolate proteins from human body fluids, the group used the IL-ABS system based on 1-butyl-3-methylimidazolium chloride (BMIM-Cl) and K2HPO4. In the IL-rich upper phase, proteins present at low levels were quantitatively extracted. The K_2HPO_4 addition to the IL rich phase (after separation) has resulted in a further phase separation and an elevation in enrichment factor was also observed. After the whole process, protein's natural structure and properties were found to be unaltered [89]. A detailed review on recent trends in protein extraction using ABS was done by Lee et al. in 2017. The review listed out almost all the studies during the last decade on IL-ABS systems for protein extraction and separation. A broad variety of cations (e.g., imidazolium, cholinium, ammonium, phosphonium and guanidinium) and benign anions (e.g., carboxylic acids, amino acids and biological buffers) were also examined for their relevance in the process. The review underlined the role of chemical structure of IL on protein partition and stability [90]. In the partition of proteins in IL-ABS, hydrophobic and electrostatic interactions as well as salting-out effects were also dominant variables. Apart from pure protein sources, several studies on separation of value-added proteins from complex media are gearing up. Latest review by Anusha et.al. on the role of ABS in sustainable extraction and separation analyzes the advancement of IL based ABS technology in the last two decades [91]. The quest and growth of research is in the right direction and will provide a new outlook to this area of research in both commercial and economic sense.

Nucleic acids are known to be the unique identity molecule of any organism and have emerged as powerful biological tool. They are carriers of genetic information and can act as a digital data storage medium in, with potential benefits such as high density, high efficiency of replication, long-term longevity and long-term stability. In molecular biology, nucleic acid extraction plays a crucial role as the primary stage for many downstream applications. Developing novel methods to extract and purify nucleic acids from various types of cells and their storage are therefore crucial. Traditionally, the purification of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) was based on liquid−liquid extraction techniques involving solvents like phenol and chloroform. These solvents are highly volatile and carcinogenic. Recent studies suggest that the efficiency of extraction and purification of nucleic acids from biological samples were increased by IL addition in comparison with conventional methods. Moreover, nucleic acids in ILs showed long-term stability and enhancement in nuclease resistance. Zaho et al. in 2014 studied the interaction pattern between ILs and DES with DNA by analyzing the available literature in the field till then [92]. According to their analysis, in the case of ILs and DESs, organic cationic part is intruding into the minor groves of DNA. Electrostatic attraction is a prominent interaction between organic cations and the DNA phosphate backbone which provides additional support for hydrophobic and polar interactions between ILs and grooves. Anions may form hydrogen bonds with cytosine, adenine and guanine bases.

Moreover, nucleic acids have got structural speciality as they are viable for electrostatic interaction, formation of hydrogen bonds as well as van der Waals interactions. These strong interactions help the DNA molecules to maintain a double helical structure in most ionic solvent system. Shi et al. analyzed the polymerized chain reaction amplification of DNA by bicyclic imidazolium ionic liquid and found that nucleic acids in ILs can be used directly in polymerase chain reaction and gene expression analysis with high efficiency [93]. Based on the unique changes in the stability of nucleic acids in ILs, highly sensitive DNA sensors have been developed. The recent trends in IL-DNA interactions got a new complexion by the emergence of magnetic ionic liquid. Incorporation of MILs has made the extraction easier, and the magnetic recovery of DNA enriched IL droplet is comparatively effortless. The reusability of MILs to different cycles was also an important achievement. Jared L Anderson and coworkers deserve a special mention for their contribution in this field. In their recent study, hydrophobic magnetic ionic liquids (MILs) with long chain tetra alkyl ammonium cations and metal chloride incorporated anions were synthesized and used as solvents for the extraction of DNA from aqueous solution. After extraction the DNA-enriched microdroplet was manipulated by applying a magnetic field [94]. Very recently magnetic ionic liquids with phosphonium cations and cobalt metal in the anion sphere has been proved to be efficient for RNA extraction in aqueous solution [95]. Cations and cobalt metal in the anion sphere have been proved to be efficient for RNA extraction in aqueous solution [95]

Apart from the discussed, many other biomolecules and bioactive components including lipids, fats, vitamins, carotenoids were successfully extracted and preserved with the help of ionic liquid assisted chemical processes [96–99]. The important hurdle to pass in the biomolecule extraction is the modification of separation strategies and the lack of techniques in IL recyclability and reuse. Emergence of MILs and new developments in DES related research have addressed this issue to an extent. Application of the mentioned techniques to an industrial scale is also important. Large scale separation and storage of biomolecules is necessary in commercial and economic sense. Once it comes to a bigger picture, a lot of practical issues can be dealt including cost effectiveness, storage capacity and purification strategies. In conclusion the development of cost-effective and more sustainable extraction and separation processes is the crucial step toward the recovery and commercialization of new and low-cost bioactive products for different chemical industries. While envisaging their widespread use soon to boost the quality of modern society, and in which ILs could have a remarkable role as alternative solvents and materials.

Impact

Human needs to open a myriad of dimensions in the advancement of research, which may also have detrimental effects on both the environment and social health. This has prompted scientists to pursue various strategies to mitigate environmental issues, especially through the use of green chemicals. In this sense, ILs have been introduced as a green solvent in different engineering areas, gas abstraction, fuel technology, cooling strategies etc. Nowadays, ILs are being used in the fuel industry in the different stages of oil production which were found to improve the efficiency of the crude oil extraction process. Similarly, the use of ILs have proved to be effective in wastewater treatment and CO_2 capture. These studies are the blueprints to prove the environmental and social impact of ILs. Apart from this the growth of ILs as a bio-extraction tool underlines their commercial impact. In short, the ILs, on account of being an environmentally friendly and cost-effective green solvent, is capable of improving the effectiveness of several processes which are much essential in modern circumstances. A detailed review of such applications and utilities of ILs can therefore be helpful for the further exploration of their uses and to unveil their hidden potential.

Conclusions

Throughout this review, we have appraised the advantages of implementing ionic liquid chemistry towards the field of environmental remediation and efficient energy consumption. These studies are highly promising and encouraging for the scientific community in a futuristic perspective. Needless to say, the effective utilization of energy sources and efficient conservation of nature form the life breath for the generations to come. Consequently, the progress of research in this domain has become an indispensable need of our society itself. While enumerating the advantages of ionic liquids, there had been some issues which were not really addressed. One major aspect among them is the toxicity study of ionic liquids. Although there have been a few studies carried out for assessing the extent by which the chemical compounds involved in them are detrimental to the nature [100,101], the focus towards this sector is not seems to be deep enough. There is still scope for a deep-level analysis in these aspects. Another major concern is that all the advantages which have been listed above are validated only on a laboratory scale. Very few ionic liquids have been tested and validated on a bulk scale and in industrial environments. As a result, we have not been able to identify the possible disadvantages which are likely to occur in the case of practical implementation of the same. Industrial level consumption of these chemicals may lead to several issues which may not even be present in a micro-level laboratory utilization, and therefore, a careful study of these issues is of utmost importance. Another important concern is their recyclability. Even though the advent of magnetic ionic liquids and deep eutectic solvents gives a new momentum to this concern, room temperature ionic liquids and other hydrophilic ionic liquids are observed to fail in delivering the intended functionality within one cycle of operation. It raises the question about the cost effectiveness of these classes of ionic liquids and may also be portrayed as indicator of a non-constructive utilization. Keeping all these shortcomings aside, one should appreciate the fact that ionic liquid chemistry, as an innovation, has greatly contributed to the field of energy and environmental engineering. It has opened a wide new window of opportunities for sustainable development. Cunning studies, evaluations, scientific analyses and discussions in this area are imperative in the future, in order to make the utilization of ionic liquids more eco-friendly and more economic.

Conflicts of interest

There are no conflicts to declare.

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