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Contents

PAST, PRESENT AND FUTURE OF THERMAL GASIFICATION OF BIOMASS AND WASTE

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Abstract
The thermal gasification has been used for nearly 200 years. At the beginning coal or peat were used as a feedstock to produce gas for cooking and lighting. Nowadays, the coal gasification is still actual, anyway, in times without fossils the biomass and waste gasification becomes more important.
In this paper, the past, present and future of the biomass and waste gasification (BWG) is discussed. The current status of BWG in Austria, Denmark, Germany, Italy, the Netherlands, Sweden and USA is detailed described and the future potential of the technology is outlined.

Keywords
gasification, syngas, biochemicals, biofuels, CHP, hybrid systems

Introduction

This year, 2020, the EU aims to reduce greenhouse gas emissions by at least 20% (compared to 1990). The share of renewable energy should be significantly increased. In transport sector, all EU countries should achieve at least 10% share of renewables. [1]

It seems that the energy transition should start in transport sector, followed by industrial one. One of the possibilities, how to reduce CO_2 emissions in transport sector is the implementation of electro cars. One could argue, that the electricity to power the vehicles will come from renewable sources, like wind power or PV and it seems that the problem could be solved in this way. However, what about aviation, marine or heavy-duty trucks? What about the material costs and energy demanding production process of batteries? Even if we skip the safety factor by batteries– explosion danger, we should mention that their life cycle is not as long as it should be. Producers suggest to use the battery for 500-1 200 charge cycles, it means a life span of an electro car of 5 to 10 years. Probably it is not necessary to point out, that the battery price contributes significantly to price of the electrical vehicle.
Another way, how to power the cars is the utilization of biomethane. This way seems to be more reasonable; the biomethane could be used as natural gas. Its properties are similar or even better as by its fossil-based "brother" and the infrastructure for it exists already. The significant advantage is for sure that biomethane is based on renewable resources. The idea to use biomethane in cars is not new, but demonstration of production in large scale was missing. Thus, the project with the aim to produce biomethane from biomass started in Sweden (GoBiGas) and will be described later in this paper.

In the period 2021-2030, a strong signal should be sent to the market by EU to encourage and support private investment in low-carbon technologies [2].
The strategic long-term vision ("2050 Energy Strategy) shows how Europe can lead the way to climate neutrality and Paris Agreement objective to keep the global temperature increase to well below 2°C and pursue efforts to keep it to 1.5°C.
To rich all these goals, the complete transformation of our energy policy and framework will be necessary. It is clear, that new political acts in many areas, e.g. industry or transportation sector could not be avoided. And, in this case, the massive support of renewable energy by the political acts will be the right way to the future. Not the reduction of energy use, but efficiency increase as well as search for new and advanced technologies and their synergies based on renewables and waste utilization will be the right direction how to save the environment for the next generations. It is also clear that not just one renewable energy source will be able to cover our energy demand, but technologies combination and share of renewable sources will be the right way.

In this paper, one of these technologies, which is based on bioenergy will be described and discussed. Thermal gasification of biomass and waste is a thermochemical process, which enables the conversion of the feedstock (biomass or waste) into product gas and by-products. From the product gas, after cleaning and upgrading, the

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synthesis gas, containing mostly hydrogen and carbon monoxide, will be produced. There are many ways of utilization of synthesis gas. It could be used for production of power and heat, liquid or gaseous biofuels, chemicals or for fuel cells. The by-products from the gasification process e.g. bio-char became very popular on the market and because of its purity it could be used in many ways, either for material use or carbon storage, which is of a great benefit.

History of gasification

The gasification process is not new. The process has been used nearly 200 years for energy production. At the beginning coal or peat were used as a feedstock to produce gas for cooking and lighting. During the World War II, the search for new feedstock because of fossil fuels shortage was necessary. The wood gas generator was developed, which was used to power motor vehicles, such as agricultural machines, trucks, buses and cars.

After the WWII, when the fossil fuels were available and cheap again, it was only Sweden, which continued working on gasification technology, furthermore, after 1956 (Suez Canal crisis), the gasifiers were in Sweden included in Swedish strategic emergency plants.

An overview on gasification applications in different time periods is shown in the table below. As can be seen, gasification technology was utilized already in pre-industrial time, anyway, the considerable development of biomass gasification can be observed in 20. and 21. Century, especially the boom of small-scale gasification units in Europe.

Table 1. Overview on gasification application in different time periods. *Source: [3]*

	preindustrial	1900-2000	2001 - today
Coal to Gas	-	Yes	Yes
Coal to liquid	-	Yes	Yes
Crude oil to liquid	-	Few	Yes
CHP IGCC with NG/Coal	-	Yes	Yes
Small scale biomass CHP		No	Yes
Large scale biomass CHP	-	No	Yes
Co firing BM	-	Yes	Yes
MSW		No	Yes
BM to syngas	Yes, for smoking food	Yes, short time mobile application	Yes
BM to liquid	Yes, for tars and chemicals	No	No
Biomass CHP with IGCC	-	Demonstrated	No
BM to SNG	-	No	Demonstrated

Following figure offers an overview on output of small-scale biomass gasification plants between 2009 and 2016 in Germany and worldwide.

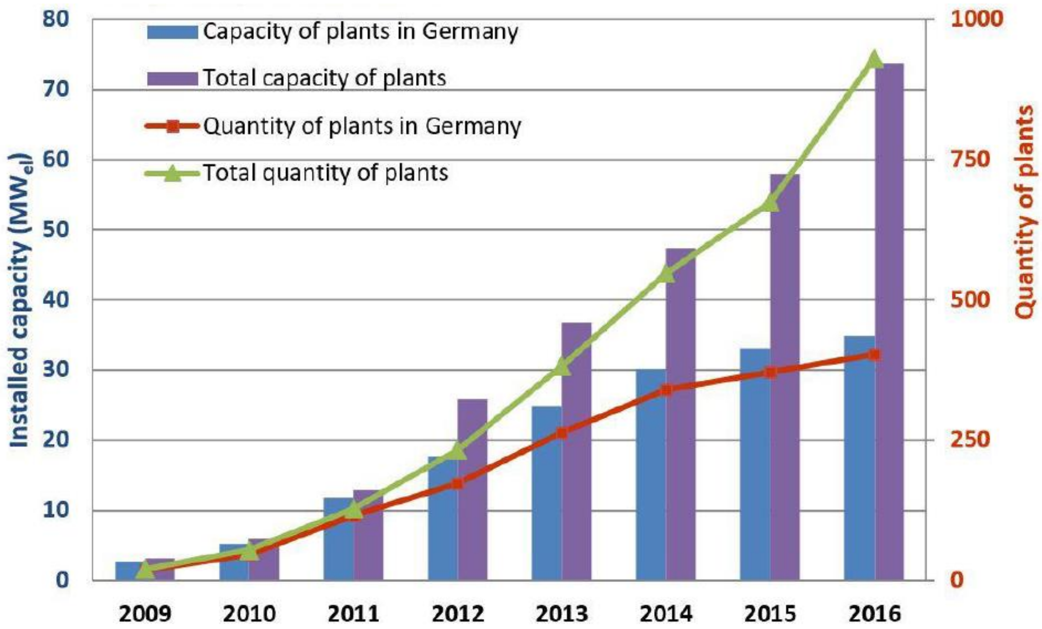

Fig. 1. Installed capacity of small-scale biomass gasification units in Germany and worldwide. *Source: [4]*

Gasification growth from 1950 to 2018 can be seen also in the following figure. The expansion after 2010 is obvious in this figure. In the cake diagram, the global syngas output by feedstock can be seen. It is clearly showed, that the syngas is produced mostly from fossil fuels.

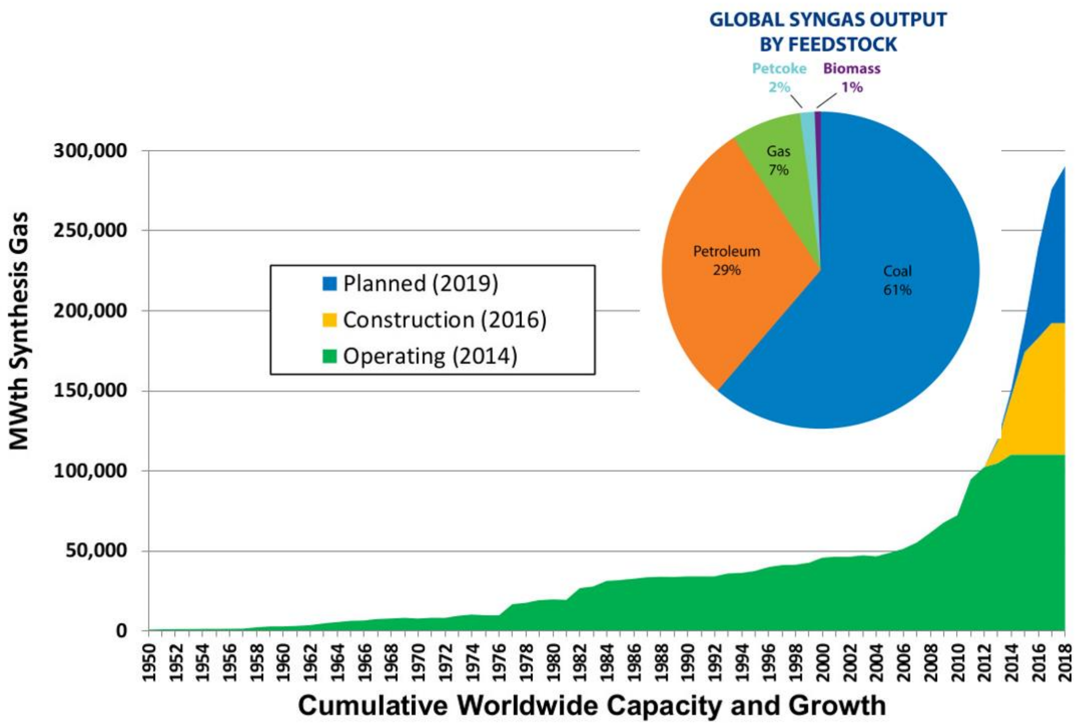

Fig. 2. Gasification growth between 1950 and 2018. *Source: [5]*

Current status of biomass and waste gasification

In this chapter, the status of thermal gasification in Austria, Denmark, Germany, Italy, the Netherlands, Sweden and USA will be described. All of these countries are/were the members in IEA Bioenergy Task 33: Gasification of biomass and waste (www.task33.ieabioenergy.com). The Task 33 is a working group of international experts with the aim to promote the commercialization of efficient, economical and environmentally preferable thermal biomass and waste gasification processes. The Task 33 works in 3-years periods. In actual triennium, the member countries are Austria, Germany, Italy, the Netherlands, Sweden, UK and USA. China will join the Task 33 probably in 2022, maybe earlier. It is also expected that Canada and New Zealand re-join the Task 33.

Austria

Research related to thermal gasification of biomass and waste takes place in Austria at Universities, research centres and private companies as well. The most important ones, which should be mentioned here are Vienna University of Technology (VUT), Graz University of Technology, University of Natural Resources and Life Sciences Vienna (BOKU), BEST (Bioenergy and Sustainable Technologies), MCI (Management Centre Innsbruck) and GET (Güssing Energy Technologies).

The research fields are very diverse. Starting with testing of different feedstock, through different gasification technologies to product gas and valuable by-products, which could be used in many different ways. The evaluations of the whole process chain are provided as well.

At Austrian Universities, two significant gasification technologies were developed during the last years, which after scaling up were very successfully implemented not only in Austria but also abroad.

The first one was FICFB gasifier (Fast Internal Circulating Fluidized Bed), which was developed at Vienna University of Technology and at the first time realized in Güssing (scheme 2001). The process will be described later in this publication.

The improved system called "G-volution" was built at VUT as the latest pilot plant for testing the whole gasification process in practice. The test plants development at VUT can be seen in the following figure.

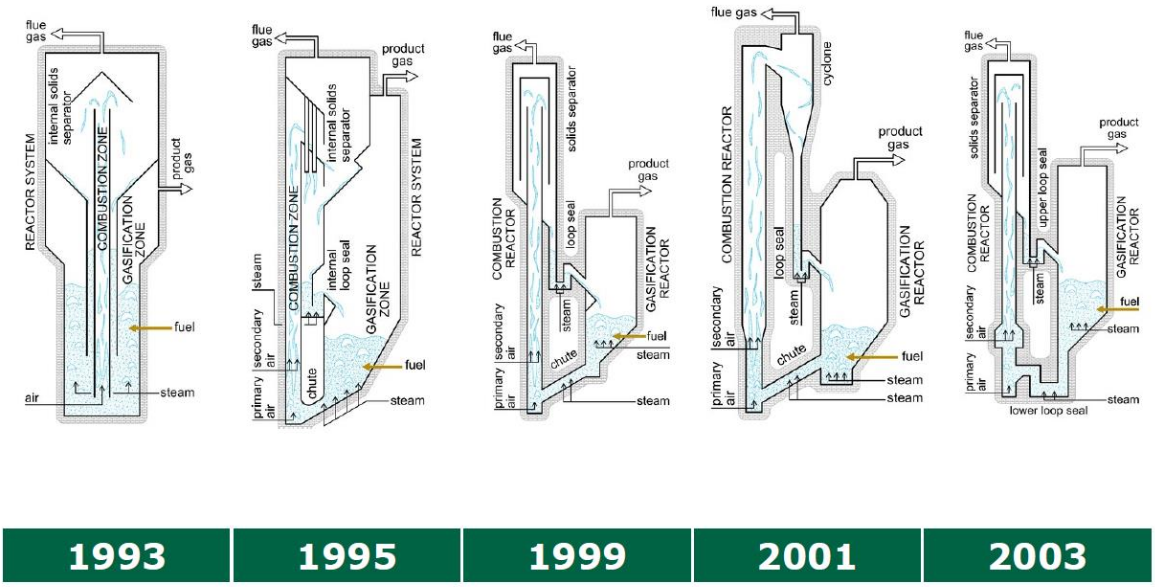

Fig. 3. Research at VUT - development of dual fluidized bed. *Source: [6]*

G-volution, a novel gasification process was developed in 2014 and since that time, many research projects were provided using this 100 kW test plant. The scheme of the reactor, which is divided into the gasification and combustion zones, can be seen in the figure below. The innovative is the gasification part of this set up, where the reactor includes several strictions. These strictions in reactor make the gas, together with fuel particles, to change their velocity several times and ensure the longer contact with bed material as well as longer remaining time in gasifier. This gasification system can be applied on bride spectrum of different feedstock such as wood, agricultural waste, coal, industrial residues etc. For improved product gas quality, the different bed materials, e.g. with catalytic effects can be used.

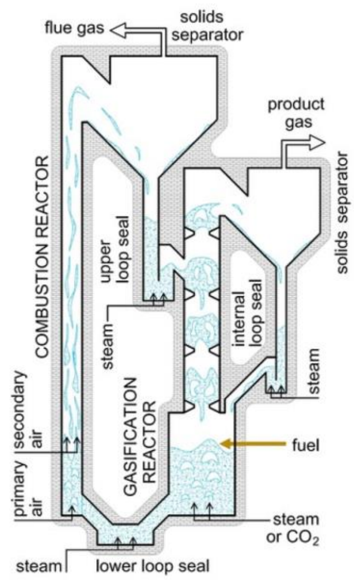

Fig. 4. Gasification system G-voution developed at VUT. *Source: [6]*

The second gasification technology, which should be mentioned here, is a staged gasification process with the floating fixed bed reactor, developed by SynCraft and MCI.

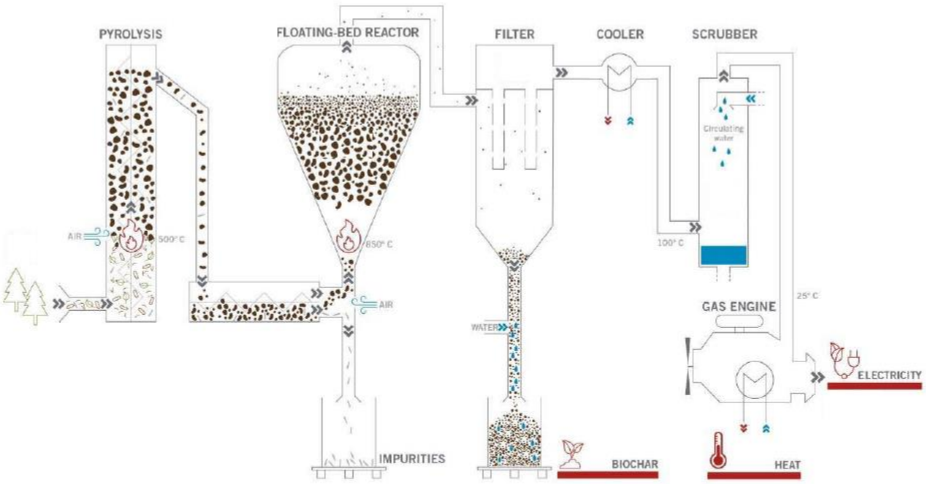

Fig. 5. Staged floating fixed bed gasification system by SynCraf. *Source: SynCraft*

The first step of the process is pyrolysis, where also the devolatilization takes place, fuel particles moves than to floating fixed bed reactor, where they are gasified. The gas, after the cleaning and cooling is used in gas machine for power production, the heat from the process can be used for district heating and drying of the feedstock. The valuable by-product is a premium quality charcoal, which is sold by company to the market. The system operates on low quality dry wood chips including bark and fine particles and overall electric efficiency due to high-tech gas engines is over 30%. At this time, there are 7 SynCraft facilities in operation and 8 further are planned/under construction. Nowadays, the implementation of many small-scale gasification projects can be observed in Austria. Opposite to this fact, it should be reported that the two biggest Austrian gasifiers in Guessing and Oberwart were shut down due to economic reasons. In Guessing, the concept of the fast internal circulating fluidized bed (FICFB) gasification system, developed at Vienna University of Technology was realised, the concept can be seen in the Figure 3 (scheme 2001). The technology of FICFB is based on circulation loop between two zones – gasification and combustion ones. The bed material acts as a heat carrier and circulates between those two zones. The gasification zone is fluidized by steam and combustion one by air, during the process remain steam and air as fluidizing agents separated. Both reactors operate under atmospheric pressure.

The feedstock coming into gasification zone is converted and nearly nitrogen free gas is produced. Not fully processed feedstock rest (char) together with ash move with the bed material (sand, olivine, dolomite etc.) into the combustion zone. Here the char is burned. In this way, the bed material is heated up and moves again into the gasification zone. The temperature in gasification zone is about 850°C, in combustion zone slightly higher, about 920°C. The scale up of the FICFB gasification process was at the first time realised in Guessing, Austria. Therefore, this demo plant can be seen as a reference plant for other facilities based on dual fluidized beds such as plants in Oberwart, Senden/Ulm, Göteborg etc. The Austrian facility was about 100 000 hours in operation and with end of October 2016 was shut down and mothballed. The reason was expiring of the feed-in tariff, supporting the economic operation of the plant.

In small scale, the main producers of gasification facilities in Austria are companies Urbas Energietechnik, SynCraft, Glock Oekoenergie, Hargassner and Froeling, which are successful in Austria as well as abroad. At the moment, many small-scale facilities are in operation in Austria, not only from domestic facilities producers, but also foreign ones.
The technology of Urbas Energietechnik, Glock Oekoenergie, Hargassner and Froeling is based on fixed bed gasification.

Urbas Energietechnik realizes CHP facilities with electric power up to 30 MWel. as biomass steam power plants. They offer also smaller units with output of 150 kWel. The feedstock are clean woodchips, with moisture content below 10%. The gasification plants are delivered as container type systems. It is a turnkey technology.

Fixed bed gasification technology based on Imbert principle offers the company **Glock Oekoenergie**. Wood chips are used as a feedstock. After drying (below 30 % moisture) and gasification the gas is cleaned and cooled down and ready for utilization in gas engines to produce electricity and heat. The company offers plants in two sizes, with output 18 kWel/44 kWth and 55 kWel/120 kWth.

Hargassner offers compact gasification units based on fixed bed technology as well. The electrical output is about 20 kW. The company was founded in 80ies of the last century and since that, time focuses of thermal conversion of biomass. They started with the biomass combustion, anyway, the gasification process is in focus now as well.

Froeling is relatively newly developed company, they first facility has been in operation since 2013. Since that time, they gasifiers can be found in Austria, Germany and Slovenia. The company is focusing on units with output 50 kWel/107 kWth.

SYNCRAFT® Engineering offers a quite unique technology, which is called floating fixed bed gasification process and was described above in this paper. Within this technology, an electrical efficiency of 30% and fuel utilization rate of 92% is possible. The company focuses not only on CHP production, but also char coal (bio char), which is of very high quality and it is therefore solved to the market, offering an additional income. The technology is a turnkey, the units are delivered with electrical output between 200 and 500 kWel.

All small-scale facilities utilize wood chips or pellets for the combined heat and power generation. In addition, the utilization of lower quality feedstock, such as waste wood could be of interest for small-scale gasification.

In Austria, also a large-scale gasification unit for waste materials (RDF) within the project **Waste2Value** will be built in 2020. The commissioning is planned for beginning of 2021. It will be a 1 MW dual fluidized bed gasification unit with improved reactor design as described above. The facility will be coupled with 300 kW Fischer-Tropsch synthesis pilot plant. A research laboratory will be a part of the side, where test rigs for production of mixed alcohols, H_2 separation, methanation will be situated.

Denmark

Talking about research in the field of thermal gasification, following research institutions and centres should be mentioned: Danish Technical University (DTU), Aalborg University (AAU), Danish Gas Technology Centre (DGC) and Danish Technological Institute (DTI).
Danish Technical University (DTU) aims to be leading the research within thermal gasification technologies in Denmark. The gasification group focuses on high efficient CHP as well as production of biofuels, such as bio-SNG or methanol.

It worth to mention two gasification systems, developed at DTU. The first one is a two-stage gasification system called VIKING. Exactly it is a three-step conversion process if also the drying would be taken into account. The feedstock comes into dryer, where the moisture is reduced using superheated steam, then moves into the pyrolysis part and finally is gasified in the downdraft fixed bed reactor. The advantage is a high-energy efficiency, which is about 93% as well as clean product gas without tar. The technology is now owned by company Weiss.

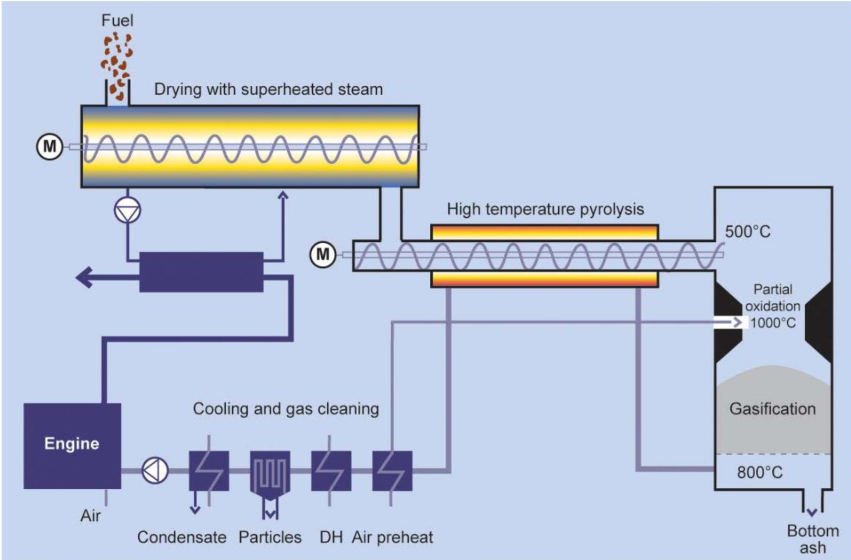

Fig. 6. VIKING gasification system developed at DTU. *Source [7]*

The second gasification system, which was developed at DTU, is called PYRONEER, which is a low temperature circulating fluidized bed technology. The advantage of this technology is the utilization of a bride spectrum of different feedstock, such as straw, manure, sludge, industrial waste etc. Furthermore, the ash from the process can be used as a fertilizer, because of lower temperature of gasification (below 730°C).
The scale up to 6 MWth was successful, the technology is owned by DONG Energy. Anyway, the facility is not in operation at the moment, it was mothballed at the end of 2015.

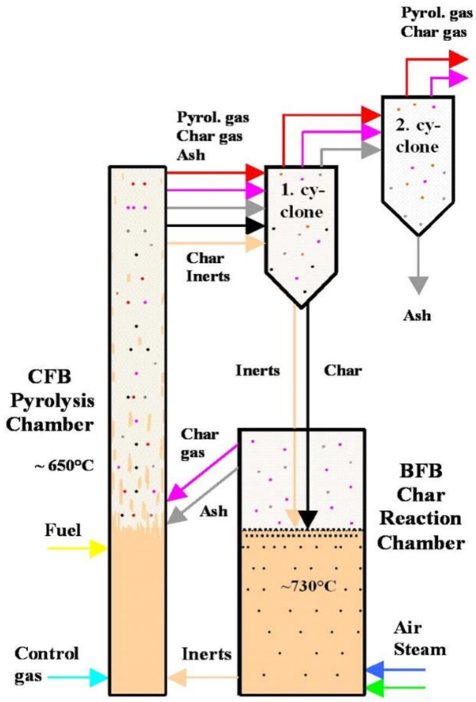

Fig. 7. Pyroneer gasifier. *Source: [7]*

Nowadays, following commercial gasification facilities are now in operation: in Harboøre, Sindal and Skive. The product gas is used for CHP applications. An overview on gasification technology, input and output, as well as utilization of the gas can be seen in the Table 2 below.

Table 2. Thermal gasification facilities in Denmark. *Source: [8]*

Project name	Technology	Input/ Feedstock	Output/ El./Th.	Usage/ Product	Start up
Harboøre CHP plant	Fixed bed - updraft	3,5 MW /forest wood chips	1 MW electric 1,9 MJ/s heat	CHP generation	1993 (CHP in 2000)
Sindal CHP plant	Staged updraft	5.5 MW /wood residues	0.8 MW electric 5 MJ/s heat	CHP generation	2018
Skive CHP plant	Bubbling fluidised bed	20 MW /wood pellets	6 MW electric 11,5 MJ/s heat	CHP generation	2008

A demoplant in **Harboøre,** which was based on developments of Babcock and Wilcox Vølund and university research, was established by Harboøre Varmeværk already in 1993.

Anyway, in 1997, after further developments, the gasifier was considered as commercial and in 2001 the plant was converted into CHP. The plant is since that in operation for 8 000 hours / year and supplies heat for the district heating and power to the net.

In Sindal, natural gas was used for district heating till 2018. To come out of the fossil fuels, the company **Sindal District Heating** searched for more environmental-friendly fuels and decided to build a Dall Energy biomass gasifier with an ORC turbine.

The technology is an updraft gasifier with partial oxidation, afterburner, thermal oil heater, scrubber system for recovery of heat and ORC unit. It is a third generation "Dall Energy Furnace".

In **Skive**, a bubbling fluidized bed (BFB) gasifier for CHP production was installed. As a feedstock, the wood pellets are used (20 MW input). Output is 6 MWel and 11.5 MWth. The heat is used in local district heating system and electricity comes into the grid.

Germany

There are many research institutions in Germany, focusing on thermal gasification of biomass and waste, such as The Karlsruhe Institute of Technology (KIT), The German Biomass Research Centre (DBFZ), Technical University of Munich, Fraunhofer Institute for Environmental, Safety, and Energy Technology (UMSICHT) and many others. Most of them are active in research of all thermal conversion processes and aim to develop an overall concept for the future energy mix, which could be employed in Germany in the near future.

KIT is a leading German research institution, where also a unique and nowadays already well-known bioliq process was developed. Research area at KIT is covering a wide range from characterization of materials to simulation of complex integrated systems.

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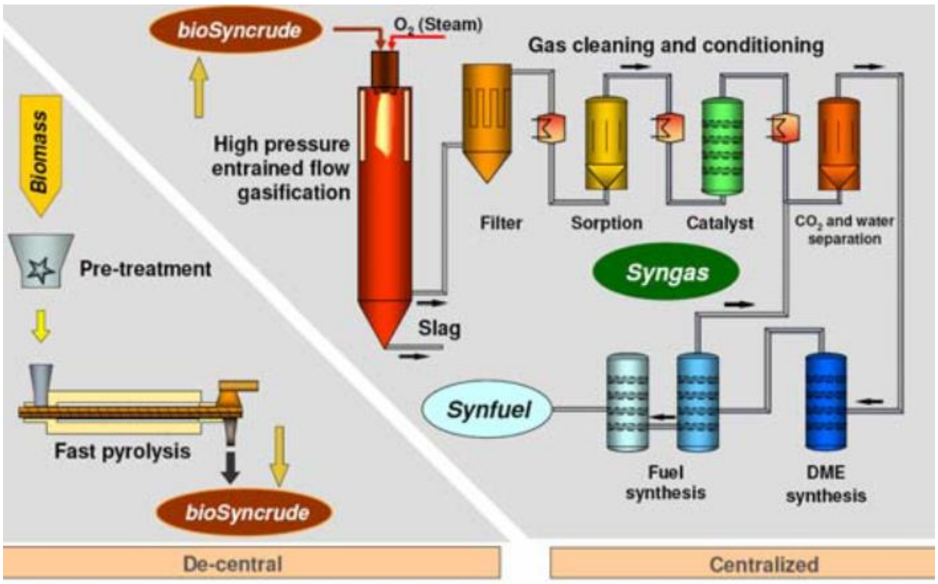

Fig. 8. The bioliq plant – process diagram. *Source: [9]*

The bioliq system, which is still in operation, consists of two different parts: de-central and central.
In de-central part a biomass (straw) is pyrolysed (2MW); in centralized part, the slurry gasification of biosyncrude takes place. The high-pressure entrained flow gasifier operates up to 8 MPa.
Both, the pilot plant for fast pyrolysis as well as a gasification unit were made in cooperation with AirLiquide E&C, Frankfurt. The hot gas cleaning in cooperation with MUT Advanced Heating GmbH, Jena and dimethylether and final gasoline synthesis together with Chemieanlagenbau Chemnitz GmbH.

The pilot plant providing a TRL level 6 is used to calculate mass and energy balances as well as practical experience with facility operation. The KIT tests there also fuel flexibility and its influence on the product quality [10]. In small scale, many companies are active in Germany. The product gas from gasification is mostly used for combined heat and power production.

On sewage sludge gasification focuses **Sülze Kopf SynGas**, a developer and producer of bubbling fluidized bed gasification systems for sewage sludge for heat, or combined heat and power applications. Their plants are fed with dried sewage sludge.

The technology of **Burkhardt GmbH**, which produces wood gasifiers since 2010, is based on co-current stationary fluidized bed. Three gasifier sizes for production of power and heat are offered by the company: 50 kWel, 165 kWel and 180 kWel. The feedstock are wood pellets. Nowadays, there are more than 240 Burkhardt operational units in Europe.

The gasification technology of **LiPRO Energy GmbH&CO.KG** is based on multi-stage gasification. The product gas is used for CHP applications, the output is between 30 – 50 kWel and 60 – 100 kWth respectively.

Spanner is well known producer of co-current fixed bed gasifiers using wood (wood chips, briquettes or pellets) as a feedstock. The output varies between 60 – 100 kWth and 30 – 50 kWel, using cascade combination it is possible couple more plants together. More than 700 operational plants could be found worldwide.

The next, well-known producer of counter- current fixed bed wood gasifiers is **REGAWATT.** In addition, here, the product gas is used for CHP applications. REGAWATT offers their gasifier from 300 – 2000 kWel and 600 – 4300 kWth respectively.

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Italy

Bioenergy research in Italy is split between seven Universities and research institutions, such as ENEA, CIRBE, CNR, Free University of Bozen, RE-CORD, SOTACARBO SPA and University of Capania "Luigi Vanvitelli". Detailed information regarding Italian research can be found in IEA Bioenergy, Task 33, Country Report Italy [11].

Research activities cover fixed bed and fluidized bed gasification technologies with facilities from laboratory scale up to pilot plants in range of MWth. Feedstock quality and analysis research focuses not only on woody biomass but also more difficult materials such as sludge, manure, rest waste etc. The next research field is a high temperature gas cleaning and conditioning, process simulations and modelling, biofuels production and life cycle and techno-economic assessment.

In commercial scale, the small-scale gasification is very popular in Italy. At the moment, there are more than 220 units in operational and further facilities are planned. The research in this field focuses also on gasification of non-woody biomass, e.g. chicken manure, rest waste etc. At the moment, there are no large-scale operational units in Italy.

An overview, how the small-scale gasification units are spread in Italy can be seen below.

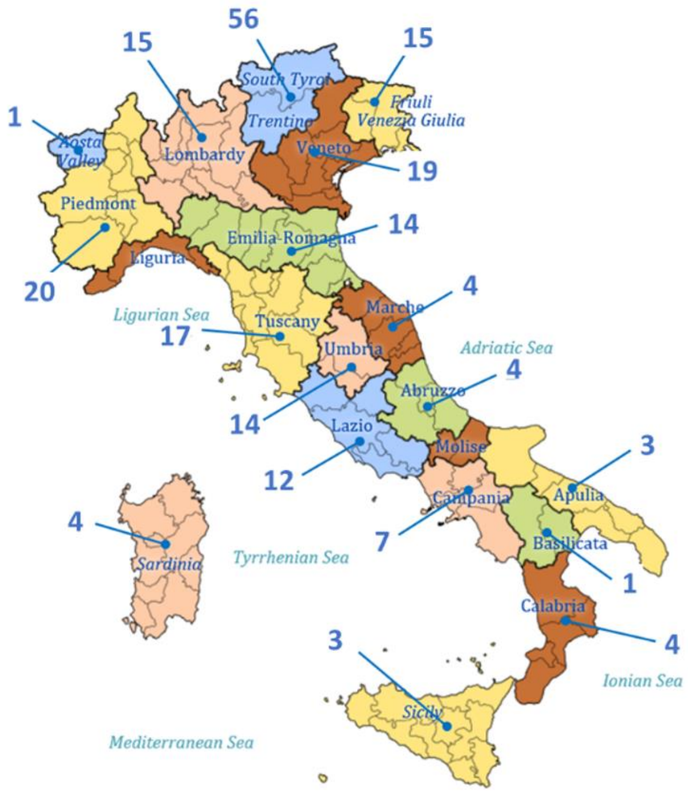

Fig. 9. Number of operational gasification facilities in each region of Italy (status 2019). *Source: [12]*

Most of the facilities are situated in northern part of the country, the power output is between 20 and 70 kWel.

In Italy, three commercial producers of the thermal gasification facilities can be found: CMD ECO20x, ESPE SRL and RESET SRL; the rest of the operational facilities come from foreign producers, mostly from Germany. An overview on Italian gasification facilities can be seen in the following table.

Table 3: Technical data of Italian small-scale gasification facilities

	CMD ECO20x	ESPE SRL	RESET SRL
Technology	Micro Combined Heat & Power	Downdraft	Containerized biomass gasification and cogeneration systems.
Output	20 kWel/40 kWth	49 kWel/100kWth	50-200 kWel
Innovation	Trigenerative purpose (electricity, heat, cooling – absorption chiller)	Product gas extremely clean, no need for filters. Total efficiency 90%	High grade biochar production
Feedstock	Wide range of biomass	Clean wood chips	Woody biomass

The Netherlands

The research in the Netherlands takes place at Universities, research institutions and private companies as well. The technology, which should be pick out is a gasification system MILENA and tar removal OLGA. Both of them were developed at ECN, now part of TNO. MILENA is a CFB gasification technology consisting of two coupled reactors (gasification and combustion zones). It was designed for wide range of fuels, from woody biomass and straw to coal or industrial waste. The technology was licenced to Thermax and Royal Dahlman. The pilot plant using these technologies will be built in Alkmaar, producing 4 MW SNG.

In the Netherlands, many commercial projects in area of thermal gasification are ongoing [13]. Some of the most important ones will be mentioned here.

Essent/RWE is an owner and operator of Amer-9 – a waste wood gasifier, which is coupled with a coal-fired power station of 600 MWel output. The facility based on Lurgi circulating fluidized bed can be found in Geertruidenberg. The waste wood is gasified using steam and air and the gas is used for co-firing. The gasifier capacity is about 85 MWth. The wood is in coal plant co-fired in two ways; about 25% of energy comes from direct co-firing of wood pellets and about 5% indirectly through a gasifier.

The thermal gasification of biomass is used also in pulp and paper industry by **ESKA**. The CFB gasification replaces here natural gas. As a feedstock paper rejects are used, the product gas is fed into a boiler. The technology supplier is Leroux & Lotz. Since 2016, when the operation started, over 20 000 tons of reject were processed.

Mavitech Green Energy is a turnkey gasification plants producer. A downdraft fixed-bed technology is used to process various manure and sludge. The product gas is co-fired to produce heat for steam production or for CHP applications. The company is also a producer of biochar (EcoChar), which can be used in many different ways.

Synova, which started as the USA company received in 2017 the right on ECN technologies (MILENA, OLGA) and resides now in the US, Thailand and the Netherlands. The focus of the company is conversion of waste feedstock into power and heat. They plan to build a gasification plant in Thailand, where the waste wood will be converted into power and heat.

Synvalor focuses on gasification of difficult fuels (wood dust, chips, grass, straw, residues etc.) to produce low-tar gas for gas engines. The aim is to rich investment point below 2 500 Euro/kWel. The technology is called Synvator®. Pilot plant with 50 kWe was built.

Torrgas focuses on biomass-to-energy and biomass-to-chemicals projects. Their aim is to be a leading provider for syngas production from torrefied biomass. They specialize on plant scale between 10 and 100 MW.

Between the largest suppliers of bioenergy facilities in Europe, focusing on technological development, the **HoSt** should be mentioned. Their portfolio spreads in many areas from anaerobic digestion and biogas upgrading to biomass CHP plants and boilers. Regarding the gasification technology, they offer CFB for boiler applications. The input is between 1-5 t/h but they offer also special plants with higher input.

Sweden

From Swedish research institutions focusing on thermal gasification following should be mentioned here: Chalmers Technical University, Royal Institute of Technology (KTH), Luleå Technical University of Technology and Lund University, where the gasification research started in 1975 focusing on oil shale gasification.

The Swedish Centre for Biomass Gasification (SFC) is a Centre of Excellence, created to coordinate and support established Swedish research in the area of biomass gasification. SFC is therefore an important national actor for developing new knowledge needed to reduce the country's dependence on fossil fuels and for reducing the net emissions of greenhouse gases to the atmosphere. [14]

Talking about the thermal gasification in Sweden, the **GoBiGas** project has to be mentioned. The project, which was initiated already in 2005 is described in detail in. [15]

The aim of the project was the demonstration of renewable biofuel (biomethane) production from biomass using thermal gasification and methanation processes. To reduce the investment risk, the project was split into two phases. It was planned to build a facility, where 20 MW of biomethane will be produced. This was the first step of the project and it should be mentioned, that this first phase was never intended as a self-sustaining project. As a second project phase, an upscaling to 80-100 MW output was planned.

As a gasification technology, an indirect atmospheric pressure gasification (DFB) from Austrian company Repotec (now Aichernig Engineering) was chosen and Finish company Valmet was selected to build up the gasification plant. Haldor Topsøe was responsible for methanation technology. The Dutch engineering company Jacobs was engaged as the EPCM contractor for the overall installation.

The mechanical completing was finished in December 2013 and the official opening of the plant was in March 2014. One month later started also the gasification process and in December 2014, the production of biomethane and its feeding into the grid began. With the continuous operation in autumn 2015, more than 90% of design capacity was achieved. Parallel to this first project phase the evaluation and preparation of the second project phase was ongoing. Anyway, in November 2015 the City Council of Gothenburg, which was the owner of the plant, decided to cancel the second phase.

In February 2018, over 1 800 operational hours were achieved and 100% of design capacity. Anyway, the sales values of biomethane had not followed the expectations, lower demand on biomethane caused by lower sales of compressed natural gas (CNG) vehicles and imports of cheaper biomethane from Denmark led to shut down and mothballing of the plant in May 2018. However, even if the facility was closed after only 5 years of operation, it was clearly demonstrated that the technology for production of biofuels from biomass works well and can be applied maybe in future, when better conditions for biomethane production will be set.

Another Swedish company focusing on production of gaseous biofuels is **Cortus Energy AB** and its WoodRoll® technology. This is a three steps integrated process, consisting of drying, pyrolysis and gasification. During this steps, the wet solid biomass can be converted into clean syngas. The process is fully allothermal and excess heat is used counter current the biomass processing. In 2011, the first plant was built in Stockholm. It was a 500 kWth gasifier, which was later moved to Nordkalk site at Köping. Based on the tests and experience with this unit a fully integrated unit has been built in 2015. It has been reported in [15] that the gasifier has been operated over 5 000 hours in September 2018, and the dryer and pyrolyzer over 2 000 hours each. Cortus Energy AB cooperates with many European companies and in 2018 a contract with Infinite Fuels GmbH was signed. The aim was to produce biomethane for the grid injection in Northern Germany. The realisation was planned in 2019. Cortus is focusing also on aviation fuels and in 2018 was it a grant from Swedish Sustainable Aviation fuel program awarded to study the integration of the WoodRoll system with a FT system producing aviation fuel.

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The next player, focusing on innovative gasification technologies is Swedish company **MEVA.** They constructed a Vortex Intensive Power Process (VIPP-system) in 2012, based on developments at LTU. The technology consists of cyclone gasifier, which is the main core. The aim was to utilize the product gas in small-scale gas turbines. Based on the evaluation of the process a pilot plant with input of 500 kWth with included gas cleaning process and 100 kWe output was built at ETC.

The thermal gasification has a long history in Sweden and not only dried biomass is mentioned to be applied in gasification process. Thus, also the **black liquor gasification** was in focus of Chemrec Kraft Recovery. The technology was based on a refractory-lined entrained bed reactor, where the material was gasified at high temperature (1000°C) under reducing conditions. The product gas was used for DME synthesis in the FP 7 Bio- ME plant. The project for DME production started in 2008 and a 4 ton/day BioDME plant was constructed, based on Haldor Topsøe technology. In 2011, the fuel (DME) was produced and used in four locations in Sweden to power ten trucks. Nearly 400 tons of DME was produced for utilization in trucks for 80 000 kms. When the project ended in 2013, the plant was moved to LTU for further research in this field.

At this time, in Sweden some further gasification based projects are planned, e.g. biomass-to-methanol facility in Hagfors (VärmlandsMetanol AB) and production of bio methane (Bio2G) [16].

USA

Within the field of thermal biomass gasification in the US, the main focus is on production of biofuels based on renewable sources. At the moment, three American companies are working on projects regarding liquid and gaseous biofuels.

The conversion of biomass using the thermal gasification process coupled with FT technology is the purpose of **Red Rocks Biofuels** project. They are constructing a biofuels plant in Oregon to produce 15 mill. gallons/y of biofuels from 136 000 tons of wood. The gasification technology is licensed by TCG Global. Fluor is responsible for syngas cleaning and conditioning and FT technology provider is Velocys and EFT. Haldor Topsoe and other companies provide the hydrocracking and fractionation technology. 40 % of the product will be jet fuel, 40% diesel and the rest will be sold to the market as a gasoline blend. Red Rocks Biofuels has an offtake agreement with FedEx. At the moment, the plant is under construction, operation should start later this year.

On bioethanol production focuses **Aemetis**, which is partnering with InEnTec and LanzaTech. The goal is to produce 60 million gallons/y using the plant, situated in California. Syngas will be produced from biomass using plasma enhanced melter (PEM) technology, which is licensed by InEnTec. This will be coupled with microbial fermenter of Lanza Tech. Primarily; bioethanol will be produced. Construction is planned for 2020.

Conversion of MSW (municipal solid waste) into synthetic crude is the goal of the **Fulcrum Bioenergy's Sierra Biofuels.** The plant in Nevada should convert about 200,000 tons/y of MSW into more than 10 mill. gallons of syncrude. The three-step process should contain pre-processing, gasification and FT synthesis. The gasification technology is based on ThermoChem Recovery International's indirectly heated fluidized bed steam reformer. The product gas from waste gasification, which will be used for FT synthesis, should fulfil defined criteria, thus the cleaning and conditioning of the gas could not be avoided. It will be therefore treated using Praxair's Hot Oxygen Burner (HOB) technology to increase the quality of the gas. By this process, the hydrocarbons and tars will be partially oxidized. It was reported that the plant should start the operation in 2020.

Thermal biomass and waste gasification in other countries

In the field of thermal biomass and waste gasification there are also many other countries, which are active in this field, but were not described in this paper, e.g. France (e.g. Gaya, BioTFuel projects), UK (a MSW gasifier (KEW) will be taken into operation in 2020), Finland (lot of research in this field, company Valmet involved in many projects), Canada, China and India. The overall data are unfortunately not available at the moment.

Future of thermal gasification of biomass and waste

The technology of thermal gasification is still further developing.

Regarding the feedstock, wood alternatives, which are cheaper but for the gasification process more complicated such as waste materials (sludge, plastics, MSW) are in focus.

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Also the purpose and utilization of product gas changes. Whereas in small-scale gasification the heat or combined heat and power (CHP) production is still dominating, in the large scale more advanced cleaning and conditioning make it possible to produce gaseous or liquid biofuels and biochemicals, which could replace fossil ones in the near future.

The third issue, which have to be mentioned beside feedstock and gas utilization, is the integration of gasification into other processes and vice versa, other processes into gasification. There are many reasons to go this way, some of them are:

- the yield of the final products and efficiency could be maximised, e.g. combination of different technologies such as wind power or PV together with electrolysis and thermal gasification for increasing of amount of biofuels production (hybrid systems)
- in southern countries, the direct solar power could be employed in the gasification process to increase the efficiency and lower the production costs
- thermal gasification can be used as a technology for balancing the electrical grid
- use the gasification technology in concepts of bio- refineries

It would be too ambitious to state; which direction the thermal gasification will develop, because this depends on many factors, but primarily on policy framework, which could encourage investors to start more projects based on bioenergy.

Anyway, the author considers e.g. waste gasification in large scale as very reasonable for the future; in this way not only waste could be disposed, but also power and heat could be produced. Another issue is the production of biofuels and biochemicals through the combination of gasification with other technologies (hybrid systems). This way, as the author believes, should be supported to come out of fossils.

Impact

The thermal gasification of biomass and waste is a technology, which can utilize a wide spectrum of different feedstock materials: not only clean biomass and forest residues, but also waste materials such as sewage sludge, agricultural residues, municipal solid waste, waste wood, straw or chicken manure.

The technology can be applied for production of renewable energy (power and heat), biofuels and bio chemicals in refinery applications or even more as carbon storage technology (biochar).

In “2030 Energy Strategy” EU countries have agreed on a new framework for climate and energy, including EU-wide targets and policy objectives for the period between 2020 and 2030. These targets aim to help the EU achieve a more competitive, secure and sustainable energy system and to meet its long-term 2050 greenhouse gas reductions target.

The strategy sends a strong signal to the market, encouraging private investment in new pipelines, electricity networks, and low-carbon technology. And this act should be also the impulse for considerable implementation of technologies based on renewable sources, such as thermal gasification of biomass and waste.

Conclusions

The significant impulse for the thermal biomass gasification progress was the World War II, when the shortage of fossil fuels occurred. In that time, the wood gas generator became very popular. As a feedstock, wood was used to power vehicles or agricultural machines. With time, the applications of thermal gasification changed. Nowadays, the power and heat is produced using mainly small-scale gasification units; at the moment, there are more than 1 500 such operational applications over the Europe, mostly in central and southern parts.

Anyway, utilization of the syngas offers not only heat and power generation, but also many other applications, e.g. production of renewable biofuels and biochemicals. Many interesting projects with this purpose started or are under construction/commissioning in Sweden (GoBiGas), France (Gaya, BioTfuel) or USA (Redrocks Biofuels). Also a lot of research work has been done/is ongoing in this field. This way of syngas utilization shows also the greatest potential for future of thermal gasification, mostly in large scale. The majority of fuels and chemicals production nowadays is based on fossil feedstock; thus, it is necessary to find alternatives for the near future.

Regarding the feedstock, waste disposal using the thermal gasification became also more interesting for investors, e.g. in the Netherlands (ESKA), in Finland (Lahti) or in the United Kingdom (KEW plant). The waste, which has a negative price seems to be of great benefit, which should be included into investment and operational costs. On the other hand, utilization of low value feedstock is still negative influencing the quality of the product gas, therefore also more expensive gas cleaning and upgrading should be taken into account. This could be anyway skipped by co-firing of the product gas, e.g. in lime kilns.

The integration of BWG into other technologies, such as paper industry, limekilns or biorefineries offers a new chance for the future. Furthermore, the combination of BWG with other technologies such as PV or wind energy (hybrid systems) provides the way of higher efficiencies and doubled amount of products [17].

The new way seems to be utilization of syngas for biochemicals production through bio-chemical conversion using specific bacteria. In this way, e.g. alcohols could be produced. Anyway, at the moment there are such application at the laboratory stage.

The great benefit offers also bio-char as a byproduct of thermal biomass gasification. There are many ways of biochar applications e.g. in agriculture as soil improver, as an addition of animal feed, or in industry as filter absorber or as energy carrier. In case, if the biochar is used as a soil improver and remains in soil for many years, we could talk also about carbon capturing, which is associated with negative CO_2 emissions.

The status of BMW in Austria, Denmark, Germany, Italy, the Netherlands, Sweden and USA was described in this paper. It can be seen that a lot of research has been done in this field. Anyway, the success and implementation of gasification projects depends on not only successful research, but also political frame conditions. The uncertain support of bioenergy from the policy nowadays does not really encourage investors, which are necessary for successful implementation of commercial projects.
The hope in this field should be the policy plan of the European Union between 2021 and 2030, so called „2030 Energy Strategy"; this could give green light to not only bioenergy, but also other renewables such as wind and solar power.

It is clear, that the thermal gasification of biomass and waste is not the only technology, which could save our world, but it should be considered as environmentally friendly, technologically proven technology, which worth to support, or to classify newly respectively. It is important to realize that e.g. the price comparison of biofuels and fossils could not be correct, if we would not take into account also the impact of the fossils to our environment.

Conflict of interest
There are no conflicts to declare

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PROCESSES OF INNOVATIONS IMPLEMENTATION INTO INDUSTRY 4.0. AUTOMOTIVE INDUSTRY STANDARDS

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Abstract
Industry 4.0 is a designation for the automation of production and labour market changes that this will bring. It is based on the boom of digitization, robotization and automation. The Industry 4.0 concept brings the benefits of increasing productivity, reducing costs and making mistakes they result from the involvement of more sophisticated machines in all company processes. The aim of this article is to present the ongoing fourth Industrial revolution (Industry 4.0.) and the impact of innovations in the company. Implementation of innovations are presented, innovation cycle itself and innovations effect on companies. Industry 4.0 makes full use of emerging technologies and rapid development of machines and tools to cope with global challenges in order to improve industry levels. Also, concepts of innovation and digitization are currently a central task for future competitiveness. Therefore, companies are establishing brand new departments focused on innovations in Industry 4.0. Industry 4.0 and digital transformation bring new opportunities in the areas of customer search, improving product offerings, and new opportunities for creating and delivering value, thus opening up new ways to create profit. First part theoretically describes various approaches to this problematic, description of four industrial revolutions and Industry 4.0. itself. Next implementation of innovations is presented, innovation cycle itself and innovations effect on companies. The last part of the article covers innovations in context of Industry 4.0. (both methods and technology) within the automotive industry. Main impact of the work is that this article puts in correlation both importance of the ongoing fourth industrial revolution with innovations in the company. It is very interesting, that these innovations with modern technologies help companies to operate more effectively.

Keywords
innovations, industry 4.0., implementation, company, production

Introduction

Technological progress has gradually created the idea of the fourth Industrial Revolution, which combines a number of key technologies and allows realizing the production in which individual machines and products communicate with each other. In modern history, every industrial revolution was characterized by the onset key industrial technologies. The first industrial revolution by invention water and steam propulsion, which revolutionized manufactory production. Second revolution then introduced electricity into production, households, and the public sector, and first serial production line. So far, the last, third industrial revolution is linked to the deployment and use of computer and robotic technology in virtually everyone areas of human activity, including industrial production [1].

Now, two hundred years after the first industrial revolution, we are at the threshold of the Fourth Industrial Revolution. Here, digital technologies and significant innovations have started development. Many of them got into life very quickly - like smartphones and mobile apps, fast internet or data storage.

Industry 4.0 is a designation for the automation of production and labour market changes that this will bring [3]. Industry 4.0 is based on the boom of digitization, robotization and automation. Number 4 marks the fourth industrial revolution, which is characterized by the full intertwining of information technology and production processes, in an intelligent way that is characteristic of autonomous machines. It is therefore largely based on

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the Internet of Things, which has brought a number of changes to manufacturing and maintenance in the industry - from reducing the production cycle to automating the maintenance of machinery and equipment [4].

In Czech Republic, Ministry of Industry and Trade deals with Industry 4.0 Initiative. According to [5] Industry 4/0/ and its impact are summarized to this definition: “Industry and the whole economy are currently undergoing a major change caused by the introduction of information technologies, cybernetic-physical systems and artificial intelligence systems into production, services and all economy. The impact of these changes is so crucial that they are referred to as on the 4th Industrial Revolution”

Although the fourth industrial revolution does not bring a completely new, revolutionary technology, we can talk about another epoch. The principle of Industry 4.0 is what make the most of current technology. Moreover, especially thanks communication of computer technology - hence machines and devices with each other. The result should be significantly modified production - the so-called high flexible mass production in a smart factory [6].

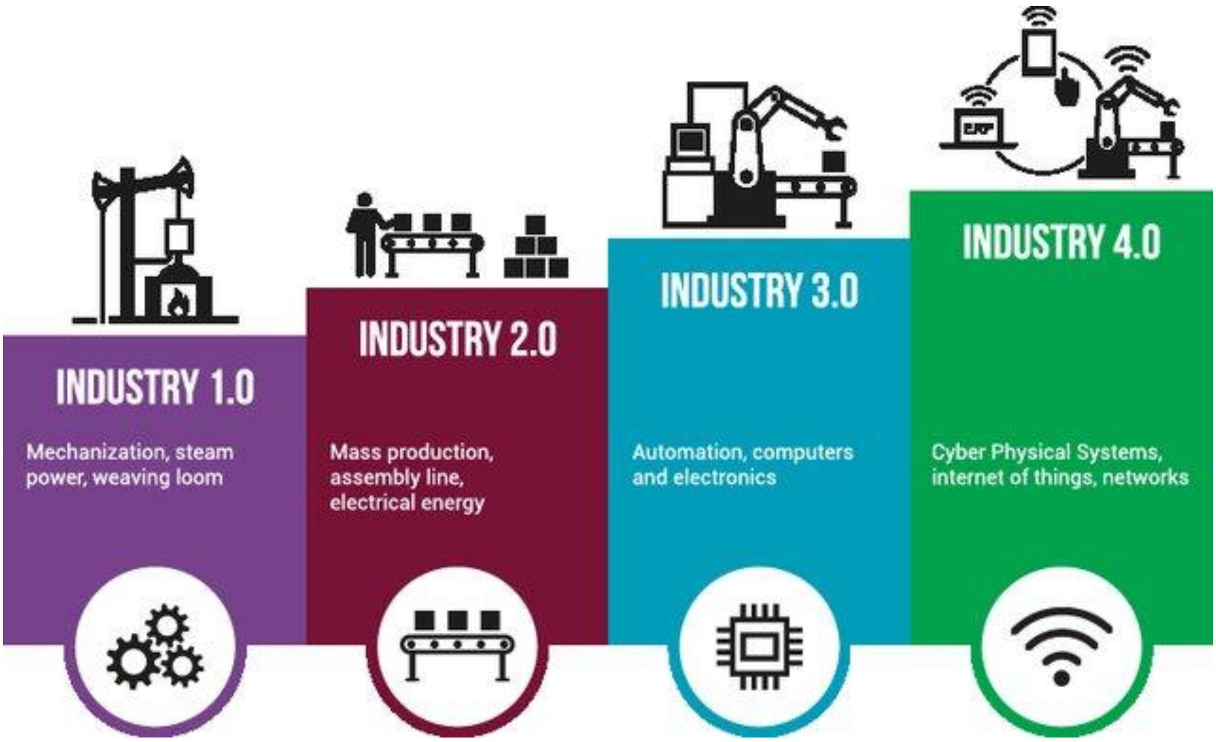

Fig. 6. Four industrial revolutions. *Source: [2]*

According to [7] Industry 4.0 makes full use of emerging technologies and rapid development of machines and tools to cope with global challenges in order to improve industry levels. The main concept of Industry 4.0 is to utilize the advanced information technology to deploy IoT services [8]. Production can run faster and smoothly with minimum downtime by integrating engineering knowledge. Therefore, the product built will be of better quality, production systems are more efficient, easier to maintain and achieve cost savings.

Gilchrist [9] in his book “Industry 4.0 The Industrial Internet of Things” highlights the 4 main characteristics of this revolution:

1. Vertical integration of intelligent manufacturing systems - that is creating networks of smart products, factories and other manufacturing systems is a necessity, because smart factories cannot work independently.
2. Horizontal integration through the global value chain of networks - probably the most important characteristic - it is the relationship between business partners and customers that should result in a global network.

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3. Engineering technology across the entire value chain - the main goal is to create a product that fully meets customer expectations. This means that Industry 4.0 takes in and includes not only the production of the product, but its entire life cycle.
4. Acceleration of production - greater emphasis is not placed on technology, which is the product but to create a better value chain.

This is possible mainly due to the expansion of 'intelligent' technology, such as cars or industrial robots, wristwatches or lawn mowers, pacemakers or ultrasonic devices. All these interconnected devices and products have three key elements in common:

- physical components, i.e. mechanical and electronic components,
- "Intelligent" components, such as sensors, microprocessors, data memory, controls, software, integrated operating systems, or visual user interfaces,
- interconnection components, antennas, interfaces, protocols and networks [10].

The latter components enable communication between the product and the cloud, i.e. the external operating system of the product. Such state-of-the-art devices are part of platforms that allow continuous data exchange between the product and the user and link information that comes from the enterprise's system to those from external sources (e.g. spatial or weather, traffic) data. This allows the following six new functional properties to be defined.

Table 4. Functional properties of Industry 4.0. *Source: [11]*

Inspection	Interconnected devices and products can control their surroundings and their activities, providing information about their performance, functions and usage.
Remote control	Users can also solve complex tasks remotely through interconnections (e.g. in hazardous or hard to reach areas).
Optimization	The combination of control and remote control also enables optimization of the entire process chain - from purchase through production to shipping. This makes it possible to improve the performance, utilization rate and availability of interconnected systems, e.g. in production or farms.
Automation	The interoperability and interplay of data control, remote control and optimization allows for further automation - devices, machines and products can adapt to the environment and user preferences, self-maintain and operate independently.
Focus on services	If businesses have data on the sale and use of their products at any time, they can react very flexibly and, for example, instead of a one-off price increase, they can raise fees that are appropriate to the product's usage. Following the example of the software industry, where a rental model (Software as a Service, SaaS) has long existed and is commonly used, traditional technology companies are now using new product-based services ("product as a service").
Individualization of the product	Increasingly interconnected and intelligent manufacturing processes, as well as additive manufacturing and 3D printing, make it possible to produce products precisely to the customer's expectations. Today, almost all products can also be offered in small batches, starting from one piece, with the same price structures that were previously only available for larger orders and relatively standardized products.

The technology base of smart factories according to Industry 4.0 [12] is based on these design principles.

1. Interoperability - ability of individual components (cyberphysical systems, people, controllers of a smart factory as such) communicate with each other using Internet of Things
2. Virtualization - creating a virtual model of a smart factory using data linking obtained from sensors that monitor real processes, with imaginary models equipment and machines; physical models of the product are also replaced by virtual ones
3. Decentralization - individual cyberphysical systems within a smart factory are able to make their own decisions
4. Real-time operation - ability to communicate between devices and products and the immediate collection and analysis of data, enabling production facilities make independent decisions and also provide detailed information about everyone's progress processes
5. Service orientation - provision of services (cyberphysical systems, human or intelligent factories) via Internet services

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6. Modularity - the flexibility of smart factories and their ability to adapt changing customer requirements by replacing or expanding individual modules.
7. Vertical and horizontal integration of production systems - vertical = information interconnection across all levels of the enterprise; horizontal = information links throughout the supply chain

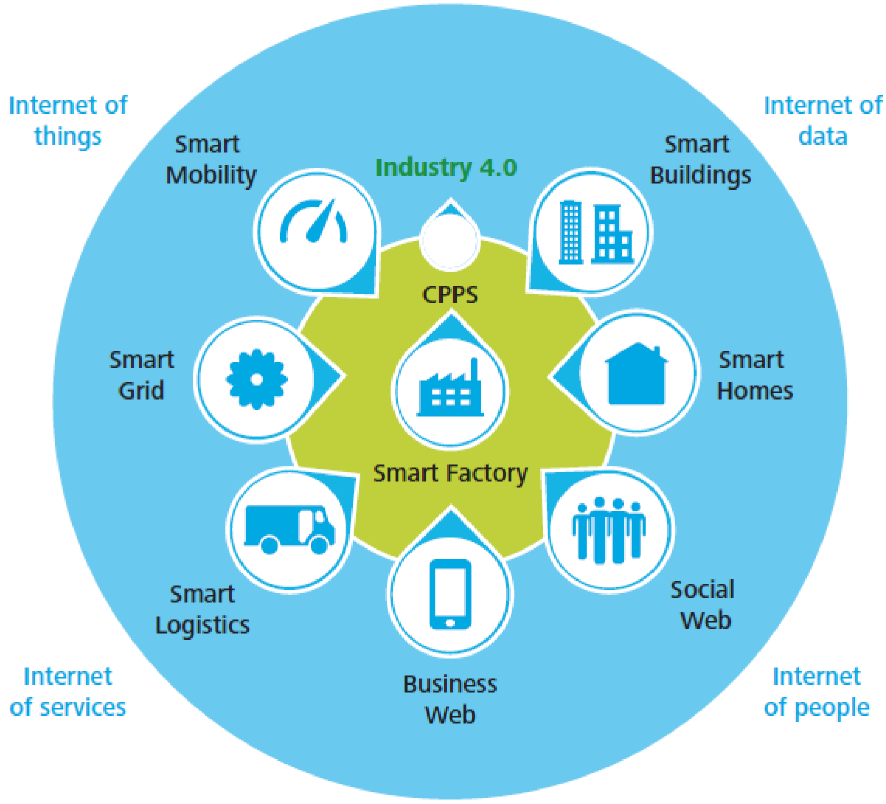

Fig. 7. The Industry 4.0. Environment. *Source: [13]*

Methods

In order to gain a better insight into implementation of innovations into Industry 4.0. company processes company innovations need to be defined. Various approaches based on latest research [2,8,12,14,15,23-25] are presented. Typology of innovations is important in order to clearly define the innovation processes.

Innovation can be the subject of any industry, it is easy to talk about, but it leads from words to actions long and demanding process [14]. Innovation can be described in a simple way as something the organization is working on at the time strives to meet one's needs. A number of authors devote to the definition of innovation and distinguish them with her gaze on her. There are definitions that are rather general but also definitions that are they focus more specifically on economics or sociology.

Invention is the name for a certain creative activity that leads to change [15]. These are mainly new ideas, ideas, and inventions. Those inventions that are realized and achieve commercial use are called innovations. Others serve only science and gain further knowledge, thoughts that lead nowhere. Inventions in the company thus represent a certain potential for creating new ideas. We distinguish between inventions absolute (brand new idea) and relative (new idea within the given organization or region). Put simply, "innovation is a realized invention".

Finding a generally valid definition of innovation is almost impossible there is no clear definition. However, from the origin of the word (innovare = from lat. refresh) it is clear that it will always be a change or novelty [16]. We can say that each author who deals with this topic creates his own definition for his own needs. The notion of innovation can be very subjective. Therefore, I would like to point out here a few with definitions of specific authors.

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One of the first to address this topic was J. A. Schumpeter, whose theory is still considered the basis of a modern approach to innovation [17]. Schumpeter considered innovations only entirely new things, which are given by promoting new combinations. So, innovation based on absolute invention. Their purpose is primarily to fill the gaps in the market, which is based on his concept of an entrepreneur as a person seeking these market gaps. Schumpeter's followers already consider innovation not only absolute innovations in the world, but also relative changes within the company.
According to [18] innovation is similarly conceived to J.A. Schumpeter, especially in relation to the entrepreneur.

“Innovation is a specific tool for entrepreneurs, a means by which to use change as an opportunity for doing business in a different area or providing different services. They can be presented as a theoretical discipline that can be learned and practically used. Entrepreneurs must purposefully look for sources of innovation, that is, changes and their symptoms, which signal opportunities for successful innovation. And they must know and apply the principles of successful innovation.”

From above mentioned, it is clear that the concepts of innovation and digitization are currently a central task for future competitiveness. Therefore, companies are establishing brand new departments focused on innovations in Industry 4.0., where topics such as enterprise-wide digitization, connectivity and new mobility solutions are the main pillars of the digital strategy. Innovations are a driving force and companies are taking advantage of the new opportunities made through digital transformations [19].

Typology of innovations

The most frequently used typology of innovations in terms of subject matter is classification according to the third version of the Oslo manual [20]. The difference from the previous version is the additional inclusion of the marketing and organizational innovation services sector. Originally, there were only technical innovations, i.e. product and process.

Table 5. Innovations typology according to Oslo manual. *Source: [20]*

Product innovations	• changes that are directly related to the product, • may include a whole new technique, may be based on a combination of existing techniques for a new application, or may be acquired through the application of new knowledge.
Process innovation	• change in the technological processes of production or in another arrangement of supply networks, • "may include changes in the facility or organization of production, or a combination of these changes, and may be obtained through the use of new knowledge", • brings positive results in reducing material consumption and labour costs, improving working conditions and the environment.
Marketing innovations	• "the introduction of a new marketing method containing significant changes in product or packaging design, product placement, product promotion or valuation", • goal of marketing innovations is to increase sales, • defined by a new marketing method that has never been used in an enterprise before.
Organizational innovation	• based on the use of new organizational methods in corporate business practices, job organization or external relations, • part of strategic decisions and the newly introduced methods in the business have never been applied before.

Innovation process

The innovation process can be understood as the path by which the innovation initiative creates a new product (or any other kind of innovation), which is further disseminated. It monitors individual phases of implementation and subsequent commercial use of innovation. The innovation process is a process that, according to Karel Skokan [21], ideally has three phases.

- Invention - is started by an idea for something new that is a concrete idea. It continues through the various phases of design, research and development. After verification of economic or market utilization, the invention leads to the adoption phase.

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- Adoption - At this stage, the first commercial use of the idea takes place. In connection with this, certain organizational, financial and investment, activities in production and sales are required. This phase is completed only when the initial invention is actually received and utilized. The introduction of the invention to the market is varied, the innovation can be adopted immediately or it can take several years.
- Diffusion - represents the phase of the innovation process, when knowledge about invention is expanding. Innovation is spreading very unevenly due to resistance, e.g. in the form of information deficits. As a result, people get information in different places at different times.

<u>Implementation of innovation into production cycle [22]</u>
At the beginning of every thoughtful and promising innovation, an innovation analysis is needed opportunities. The innovation cycle consists of seven basic phases that are grouped into three stages.

1. Stage of strategic preparation of innovations
    a. Phase 1. Innovation forecasting - analysis of state and tendency of innovation, direction of innovation in the organization in the long run. The output is innovative ideas.
    b. Phase 2. Innovation concept - formulation of the main objectives through conceptual management innovation and setting out basic strategies. The output is innovative programs.
    c. Phase 3. Innovation planning - preparation of plans that include preparatory stages innovation plan in the medium term, implementation of conceptual intentions into the plan of creation of innovation plans, selection and inclusion of innovative actions, innovation plan breakdown. The output is a plan of development projects.
2. Stage of innovation solutions
    a. Phase 4. Planned solution of innovation - research and development solution of innovative actions, specifying their economic impacts and managing the progress of these actions, preparation production, import, supply, human resources and post-production design services innovative actions.
3. Stage of innovation realization
    a. Phase 5. Introducing Innovations into Production - Capability Verification Ready innovative actions in operating conditions. Measures for optimal implementation realization outputs, reaching the projected parameters of the innovation action.
    b. Phase 6. Permanent operation - use of implementation outputs of innovative actions, in specified scope and technical-economic lifetime, maintenance and gradual rationalization of implementation outputs. Complex evaluation innovation actions and comparison of original plans with their implementation, efforts further achieve the original intentions according to the knowledge of implementation and initial operation innovated production.
    c. Phase 7. Diffusion phase - commercialization and promotion, marketing [22]

The scientific literature does not define a uniform methodology for evaluating innovation, because it is a very unique issue that differs in many aspects across companies. Still, it would the assessment of innovation should not be forgotten. Each project manager should first set a target innovation, according to the objective and the nature of the company to set important evaluation criteria and compared with the results achieved.

Results and discussion
By implementing the abovementioned elements of the Industry 4.0 concept, by innovations the following improvements would be expected:

- Eliminate errors and delays in production due to late transmission of change information between sections, such as design to purchase, technology to production, from purchase to assembly,
- Reducing the number of defective products, manufactured parts according to invalid documentation,
- Increase machining productivity by utilizing real machine behaviour data during activities,
- Improve planning accuracy and planning changes based on already verified similar orders,
- Increased assembly productivity due to minor changes to the parts produced resulting from information about problems and shape change suggestions when installing previous parts,
- Reduce the cost of product design changes based on requirements production and use.

Based the company wants to prepare for the management of new tasks in the field of digitization, connectivity, new mobility and autonomous management. Innovations take place continuously. The following table No. 3

however gives a simple overview innovation related to Industry 4.0 that are in the automobile factory.

Table 6. Industry 4.0. innovations in automotive. *Source: Own processing*

Title	Description	Benefits
3D printing	Production of functional models' vehicles, pressure production injection molds aluminium casting, printing prototype vehicle parts from plastic or plastic components or metal.	Reduced production time pre - production wagons and components, production of parts with complicated internal shapes, financial savings when production start-up.
Drones in logistics	Use of equipped drones' camera during logistics inventory of outdoor packaging areas and monitoring areas.	Time saving, full flexibility in air benefit other perspectives and the associated improving ergonomics.
Intelligent conveyors	Installation of RFID chips and several sensors on each hinge body, for purpose checking its status and reporting wear of rollers, drive, insulation wear carbon etc.	100% inspection of hinges body, instant bad article identification the whole chain of hinges, Reduce / eliminate downtime.
Electronic Gloves	Electronic Glove with implemented scanner for data recording or control material.	Increase ergonomics, data collection, control of manual operations.
Robotic hand	Cooperating robot, testing lifetime and so-called haptics car interior buttons.	Precise tuning a long-term button testing, easier haptics setup and acoustics.
Simulation of paint shop in virtual reality	Display of paint shop in virtual reality using HTC Vive glasses for preventive purposes detection of a possible collision car body with paint robots during paint application.	Early prediction and detection collisions, downtime, time savings and of new costs painting programs.
Vibromonitoring	Early diagnostics of the end rotational lifetime (high speed I slow speed) and linear bearings on framers. Cranes for achieving maximum geometric accuracy	Time savings during downtime seizure of bearings and preventive maintenance.
Virtual Training	Supplement to the training of workers directly on the wagon assembly line by simulating errors and faults.	Save time to training workers during launch of new models and equipment.

The Industry 4.0 concept brings the benefits of increasing productivity, reducing costs and making mistakes they result from the involvement of more sophisticated machines in all company processes. Of course, there are some possible threats. More intensive integration of information technology into a complex system companies are threatened by cybercriminals. These could become part of an illegal competitive buoy. Only in the event of a few hours of failure do companies face major downtime and financial losses. Security systems companies are constantly developing new protection software, but crime is always one-step ahead. On the scale of large companies, there is a risk to the national level economy.

Employment is also an inherently affected area. Talking on the replacement of employees with more efficient machines and is expected to remain in companies mainly programming, maintenance and administrative positions. It is certain that this will be the case to occur gradually, and therefore current employees will have time and space to retrain, to do so it is necessary for the government to prepare the company for these changes, labour market and social policies.

Economic Impact

This manuscript demonstrates an impact of the innovations implementation Industry 4.0. principles, development of new products and services that improve productivity, efficiency, resilience and sustainability mainly in the automotive sector. At the end of the article, successful implementation is demonstrated by the development of future technologies in automotive and mechanical chemistry.

Conclusions

The introduction of new technologies and supply of innovative products are no longer enough for companies to remain competitive or to gain a sustainable competitive advantage. We are in a time when global trends, led by digitization, are dramatically changing the business environment. To ensure long-term success, companies need to rethink and innovate their business model. Industry 4.0 and digital transformation bring new opportunities in the areas of customer search, improving product offerings, and new opportunities for creating

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and delivering value, thus opening up new ways to create profit. For companies to survive, it is essential that they respect these changes and adapt their business models to them.

Conflict of interest
There are no conflicts to declare.

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CONTRIBUTION TO THE PRODUCTION AND USE OF BIOMASS-DERIVED SOLVENTS – A REVIEW

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Abstract
In this review, key processes for the synthesis of greener or more sustainable solvents derived from renewable sources (saccharides, lignocellulose and triglycerides) are discussed. It is shown that a series of platform chemicals such as glycerol, levulinic acid and furans can be converted into a variety of solvents through catalytic transformations that include hydrolysis, esterification, reduction and etherification reactions. It was also considered several aspects of each class of solvent regarding performance within the context of the reactions or extractions for which it is employed.

Keywords
glycerol, glycerol alkyl ethers, levulinic acid, alkyl levulinates, γ-valerolactone, 2-methyltetrahydrofuran

Introduction

In the last decades, there has been an increasing effort to reduce the use of petroleum-derived chemicals and fuels in order to decrease environmental pollution and to counteract global warming [1,2]. Innovative strategies for the sustainable obtaining of these products has focused on using renewable raw materials [3]. Biomass is an ideal alternative to fossil resources, being triglycerides, lignocellulose and saccharides the main classes of feedstock that can be used for the production of greener biofuels and chemicals [3,4]. The conversion of these raw materials into valuable products is usually carried out by subsequent transformations of several biomass platform chemicals, such as saccharides (glucose and xylose), polyols (sorbitol, xylitol and glycerol), furans (furfural and 5-hydroxymethylfurfural) and organic acids (succinic, levulinic and lactic acids) [5,6]. The great advantage of biomass platform chemicals is that they are functionalized compounds, allowing its further conversion into more valuable chemicals through a lower number of steps when compared to compounds derived from fossil sources, which are essentially unfunctionalized alkanes [4].

The fine chemical and pharmaceutical industries produce different complex molecules, which usually require large amounts of solvent for their synthesis. In addition, extractions and purifications also depend on solvents, in which large excesses are needed to achieve suitable product purity. Nonetheless, solvents are essential for many chemical processes and have great effects in organic chemical reactions [7–9]. The exceeding consumption of non-renewable and toxic solvents poses risks to both human health and the environment. Therefore, biomass-derived solvents are good candidates to overcome the aforementioned issues [10,11].

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Biomass-derived solvents starting from platform chemicals could be obtained by several processes, such as fermentation, hydrolysis, reduction, etherification or esterification. Examples of these compounds are furfural, 5-hydroxymethylfurfural, levulinic acid and alkyl levulinates, γ-valerolactone, 1,4-pentanediol, 2-methyltetrahydrofuran, as well as, glycerol and its derivatives [12]. Besides coming from renewable sources, a series of characteristics are required so that a compound can be called green. The concept of green solvents is strongly related to the principles of green chemistry that aims to minimize or eliminate the use and generation of hazardous substances, while reducing energy consumption and moving toward cleaner and sustainable production from renewable sources [1,10]. It is undeniable that a green solvent must reduce health and environmental damages; however, there are several evaluation criteria to be considered, including non-toxicity, low volatility, high boiling point, biodegradability, easily recycle and ability to dissolve a wide range of compounds [12]. In this review, the chemical transformation systems and the solvents properties are critically considered in order to call the compounds as green solvents.

Environmental and economic aspects

The development of new biomass-derived solvent can be assessed by a guide created by Jin *et al.* [9]. The authors proposed a 10-step method, which are (1) identify the conventional solvent to be replaced; (2) select potential replacement candidates; (3) *in silico* modelling properties; (4) identify a green synthetic route; (5) optimize solvent production; (6) test physical properties; (7) assess performance and toxicology; (8) techno-economic assessment; (9) evaluate solvent greenness and (10) life cycle assessment. This framework is very helpful to qualify the new solvent candidate with the required properties of a green solvent and to potentially meet any required regulations. It is important to note that intermediate steps involve the careful optimization of synthetic pathways, making use of green chemistry principles, consideration of solvent toxicological testing, and final steps of more time-consuming life cycle assessment (LCA) studies. The LCA uses data acquired from secondary sources, such as databases, literature references and simulations, also, it considers the entire life of the products and raw materials [10].

The chemical industry is claimed to consider renewable sources and the valorization of wastes as the primary source of sustainable solvents toward reducing environmental impact [13]. However, some developed methods can sometimes be at odds with this goal, because researchers rarely consider the economically and environmental effects of scale up the manufacturing processes. There are a number of efficiency considerations that rule the viability of using a solvent in a given application, including both application-specific technical factors (yield, for example) and process-specific economic factors (solvent cost, for example) [14,15], along with more general considerations such as availability, scale, and disposal methods, as well as corrosion, thermal stability and toxicity concerns [10].

The choice of the compound to replace a "non-green" solvent should involve, besides the aforementioned factors, its properties in use. In some cases, the "green" solvent could lead to a lower yield of the product and create a large amount of waste that require more energy in recovery. That is why, one strategy proposed is to recovery and reuse the solvent so the process costs are minimized. Hence, the solvent stability needs to be considered in the selection of a substance that it is capable of supporting several consecutive reactions. In addition to environmental aspects, the sustainability of a process must involve economic aspects, since the cost of the implementation of a new technology can harms the adoption of the process. The requirement to change equipment is an issue for industries that aimed to adopt new greener technologies. Also, if it is a pharmaceutical industry the process should be able to attend to the regulation demands for final product quality [11].

The wide variety of biomass-derived solvents should be economically sustainable, supplied at competitive prices and industry-scale volumes. For these reasons, economic considerations can help to shape technical aspects of solvent production in order to make the chemical processes more sustainable. In addition, the solvent must have dual roles, as a reagent, lead to higher quality products, reduce the number of synthetic steps, reduce byproduct formation and improve product separation [11]. Therefore, the evolution from a traditional linear economy to a circular economy is necessary for sustainable production in all future chemical processes to advance. The circular economy is related with the recovery and regeneration of resources during process design, which consider the application of the biorefinery concept, also, recovery and reuse, minimizes impact on ecology and health. Thus, these factors strongly guide the technical and economic decisions in the development of engineering projects and in the improvement of existing plants [10,16].

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Glycerol

Glycerol or 1,2,3-propanotriol (Fig. 1) is the simplest of the triols, which was discovered in the year 1783 by the chemist Carl Wilhelm Scheele through his experiments that reacted naturally occurring oils with alkaline materials. From that date, this compound has been used in several applications, notably Alfred Nobel's discovery of nitroglycerin production and its adsorption in diatomite, a compound widely used as an explosive and popularly known as dynamite [17,18].

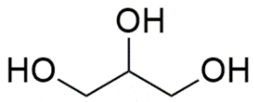

Fig. 1. Chemical structure of 1,2,3-propanotriol or glycerol. *Source: Authors.*

The physical and chemical features of this triol are that it is a sweet-tasting hygroscopic liquid that can form azeotropic mixtures and, when pure, it is odorless, colorless, viscous at room temperature and it has a high boiling point (290 °C) at atmospheric pressure. Still, glycerol has useful properties to be used as a solvent due to high miscibility in water and in short chain alcohols, but as expected its high polarity may have limited application since it is insoluble in hydrocarbons, halogenated solvents and aliphatic fatty alcohols [18–21].

The large applicability of glycerol as solvent drives the demand for this compound, which can be obtained naturally from oils and fats in amounts in the range of 8-14% w w^{-1}. In the case of its industrial production, the most well known route is from a fossil propylene source. However, other methods are also used in its synthesis, such as sugar fermentation, high-pressure hydrolysis of fat triglycerides, saponification or transesterification of triglycerides [17,20]. Among the glycerol obtaining pathways aforementioned, Fig. 2 shows the scheme of transesterification of triglycerides, common in biodiesel industry, that has increased its production over the years.

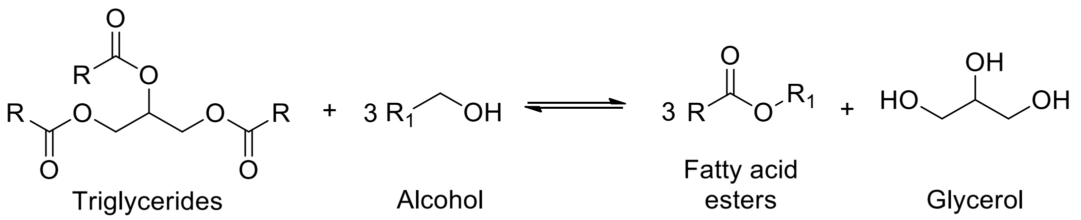

Fig. 2. Transesterification reaction used for the synthesis of alkyl esters and its coproduct glycerol. *Source: Authors.*

In 1995, the amount of glycerol obtained by the oil transesterification process for biodiesel production was responsible for abandoning of the traditional production routes of this compound, such as from polypropylene. This is because glycerol production increased per year, which resulted in a decrease in its prices. Besides that, its use can be part of the circular economy issue through its *in natura* use or obtaining other products with higher added value [22].

In the case of glycerol without modification, some studies have shown that it can be efficiently used as solvent to accelerate some synthesis processes, because in addition to being biodegradable and highly hydrophilic, glycerol is widely available, inexpensive and do not require special manipulation and storage. It is also considered a green solvent that has low vapor pressure, polarity similar to dimethylsulfoxide (DMSO) and dimethylformamide (DMF) and dielectric constant of 42.5 (at 25 °C), which is compatible with most inorganic, acids, bases, organic compounds and enzymes that are poorly soluble in water [23–25]. In contrast, the purification of compound is easiest by simple extraction because different hydrophobic solvents, such as ethers and hydrocarbons, which are immiscible in glycerol [23–26].

Since glycerol forms crystals at <17.8 °C, its application as solvent is limited in low temperatures. Thus, depending on the reaction temperature, the choice of glycerol as a solvent may not be suitable, because at temperatures below 60 °C, this liquid is viscous and may hinder the phase transfer in the system [27]. Between of advantages, this green solvent could be used at high reaction temperatures without enhances the system pressure. Moreover, the products separation process can be feasible by distillation due to the high boiling point of glycerol or by liquid extraction when hydrophobic compounds are applied in the reaction. Due to its high versatility, glycerol is used in over 2000 industrial applications, the most important being in the pharmaceutical sector as an additive for the manufacture of personal care products (e.g. toothpaste) and cosmetics. Furthermore, because of its safety LD 50 (oral rat) = 12600 mg kg^{-1}, it is a good choice as solvent for application in product carefully controlled. In addition, it can be widely used as a food sweetening additive, as a tobacco wetting agent, in the production of fuel and soap additives, pulp and paper manufactures and through its functionalization can be obtained alkyl esters, polyethers and resins [17,25].

After Wolfson's group reported the first work that efficiently explored reactions like Suzuki, Heck and hydrogenation using glycerol as solvent in 2006, many researches are involved in the use of this compound [24]. Jérome *et al.* [28] applied glycerol as a solvent in aza-Michael reactions between amines and β-unsaturated compounds to obtain β-amino acids. The authors observed that glycerol can act at the system interface by accelerating the rate of reaction possibly by transition state solvation and tolerating more hydrophobic compounds in relation to reactions that employ water as a solvent. For instance, the reaction of *p*-anisidine with butyl acrylate at 100 °C during 20 h showed a yield increase from 5% to 82% by replacing water by glycerol as solvent.

Radatz *et al*. [29] carried out condensation reaction of *o*-phenylenediamine with several ketones and aldehydes to produce benzodiazepines and benzimidazoles using glycerol as solvent. Initially, the reactions performed in the absence of glycerol were unsuccessful and using glycerol at room temperature achieved only 20% yield in 24 h. The problem not mentioned by authors was the poor mass transfer of glycerol in room temperature that probably limited the contact between reactants. However, by employing temperatures of 60 °C and 90 °C, in which this problem is negligible, yields of up to 97% of the isolated product was attained in 4 h. In addition, product recovery was performed with simple liquid-liquid extraction using ethyl acetate/hexane and glycerol was only vacuum dried and reused for 4 cycles without significant yield losses. Several other studies demonstrate the application of glycerol as a viable solvent in synthesis processes [24,30].

A reaction aqueous medium containing glycerol was used by Meyer *et al.* [31] for metallaelectro-catalyzed C–H activation. Usually, this reaction is made by applying costly and toxic oxidants, besides that fossil-derived compounds as showed in C–H/N–H alkyne annulation [32]. So, in the Meyer *et al.* [31], the authors performed the same reaction using glycerol that has a better conductivity in relation to other usual solvents such as of this reaction. In Fig. 3 it is demonstrated the scheme of this process, where glycerol/H_2O proved to be a good solvent system in organic electrochemistry achieving 96% yield in the best condition. That was the first work reporting electro-enabled C-H activation using biomass-derived glycerol.

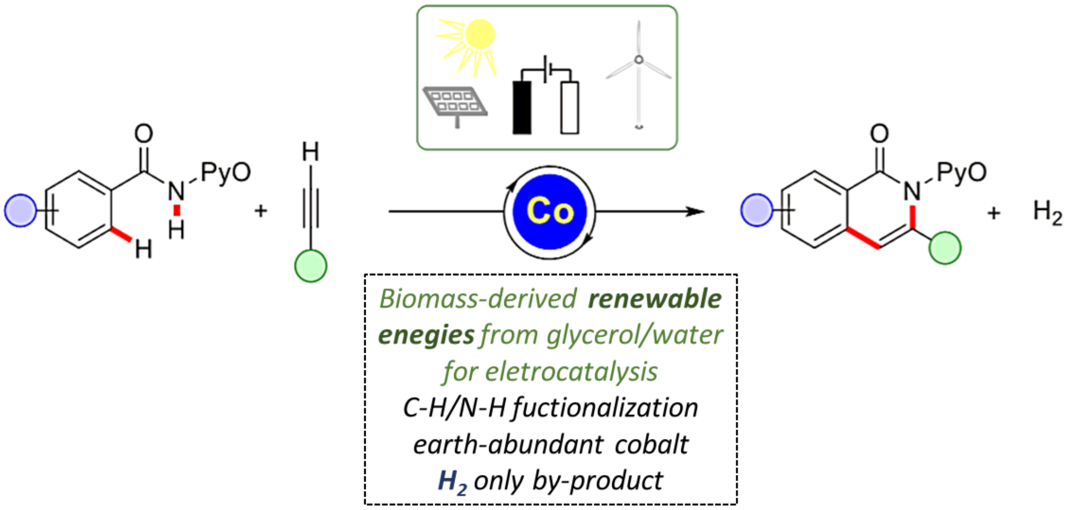

Fig. 3. Process of organic electrochemistry to C-H activation under solar and wind energy. Adapted from *Source:* [31].

Deep eutectic solvents (DES) using glycerol were reported by Li *et al.* [33] that studied the cellulose extraction from Okara by the use of three different complexing agents, choline salts in oxalic acid, in glycerol and in urea, via one-pot system. In this study, the authors investigated the structure and the properties of cellulose nanofibers obtained. Under the same homogenization conditions on a solid to liquid ratio of 1:20, at 100 °C for 30–120 min, with a stirring speed of 40 r min^{-1}, the deep eutectic solvents prepared with glycerol and Choline Chloride was more favorable for homogenization treatment. Therefore, it was suggested that this route has potential to replace the traditional pretreatment process, mainly because it is fast and improves the pretreatment efficiency, concomitant with the decrease of environmental pollution.

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Due to the properties of glycerol, which evaporates without decomposition [34], reactions have been carried out in microwaves and ultrasound to convert it into other compounds or using directly it as a solvent [23]. Balaraman and Rathnasamy [35] performed the extraction of quail eggs immunoglobulins by chromatography with specific deep eutectic solvents. Such solvents were synthesized using quaternary ammonium salts (bond hydrogen acceptor) and glycerol (bond hydrogen donor). After this, an ultrasound assisted liquid-liquid microextraction was performed and higher density solvents presented the highest extraction capacity. The authors achieved through the response surface graph built that 65 mg mL^{-1} (85% yield) could be recovered in the optimal condition of 12 min three-dimensional ultrasound at 35 °C with DES concentration of 85% (v v^{-1}) and sample load of 75 mg mL^{-1}. Despite using glycerol for the synthesis of DES, the work involved the use of irritable and toxic compounds (benzyltrimethylammonium chloride), in addition to do not mention the solvent reuse, which is important in the green chemistry concept.

Kulturba *et al.* [36] performed the DES synthesis using glycerol or ethylene glycol as hydrogen bond donor and citric acid as hydrogen bond acceptor in the molar ratio of 4:1, respectively. In this case, 9.36 mg of anthocyanin recovery from *Hibiscus sabdariffa* was achieved in 180 s and 90 °C when using DES from ethylene glycol in relation to only 5.44 mg of anthocyanin total founded to DES from glycerol. This could be attributed to the lower viscosity of ethylene glycol in comparison to glycerol, which probably allowed for better sample diffusion. In this context, more investigations are need to found better conditions to use DES from glycerol to extraction processes in microwave, because it is a solution eco-friendlier.

Another great applicability of glycerol was recently related to lignin fractionation. Usually, many solvents have been used to fractionate lignin such as ethyl ether, methanol, methane chloride, dichloromethane, n-butyl alcohol and other. However, the extraction process with several organic solvents is costly and harmful to the environment, despite being efficient. Glycerol was used in lignin fractionation by Liu *et al.* [37]. In the first step, corn straw was treated by steam explosion, and the residue went through a process of enzymatic hydrolysis. The enzymatic hydrolysis residue (EHR) was exposed to the alkaline extraction, followed by separation of soluble (EHL) and insoluble parts. After this, 20.00 g glycerol-ethanol solution (3:1, w/w) was added to 1.00 g de EHL, magnetic stirrer at ambient temperature until dissolution, centrifuged to move the insoluble lignin and obtained the sequential fractions. In this work was possible recovered lignin with different molecular weight and while decrease in its heterogeneity. The authors carried out the extraction of lignin as showed. Moreover, the mixture of 3:1 glycerol:ethanol (v v^{-1}) was recycled and reused, but the color of these compounds changed during the process due to contaminants from the extraction.

Although the literature points out that glycerol can be used in the presence of acids and bases, the presence of three hydroxyls in its structure (Fig. 1) may be important reactivity points, in addition to their coordinating properties, which can disable organometallic compounds limiting its application as inert substance [25,38]. Therefore, several modifications of glycerol have been studied in order to increase the applicability, as shown in the following section.

Modification of Glycerol

Glycerol applications in other areas include its use as a wetting agent, because its high viscosity gives greater consistency to the products and it is rapid heat transfer medium, also; it can be lubricant as it remains fluid at temperatures above 17.8 °C and is relatively resistant to oxidation. However, its properties may also restrict its application, since this triol is highly viscous at room temperature and has low solubility in hydrophobic compounds and gases. On the other hand, microwaves or ultrasound may be employed in an attempt to mitigate these issues, because in relation to conventional heating (heating plates, blankets) the use of microwaves enables higher heating rates and greater energy absorption by reactants or solvents, which results in improved mass transfer in the system. Thus, when using heating sources like microwaves, no temperature gradients or localized overheating occur and, therefore, there are advantages in the chemical modification of compounds, for example in the glycerol functionalization [23,39–41].

The chemical modification of glycerol aiming its absorption by the industry has been increasing and this compound is denominated a key raw material of many industrial chemical processes. Therefore, as can be seen in the Fig. 4, glycerol can provide a wide range of products, which are resulting of dehydration, oxidation, esterification, acetylation and etherification reactions [17,23,25,42,43].

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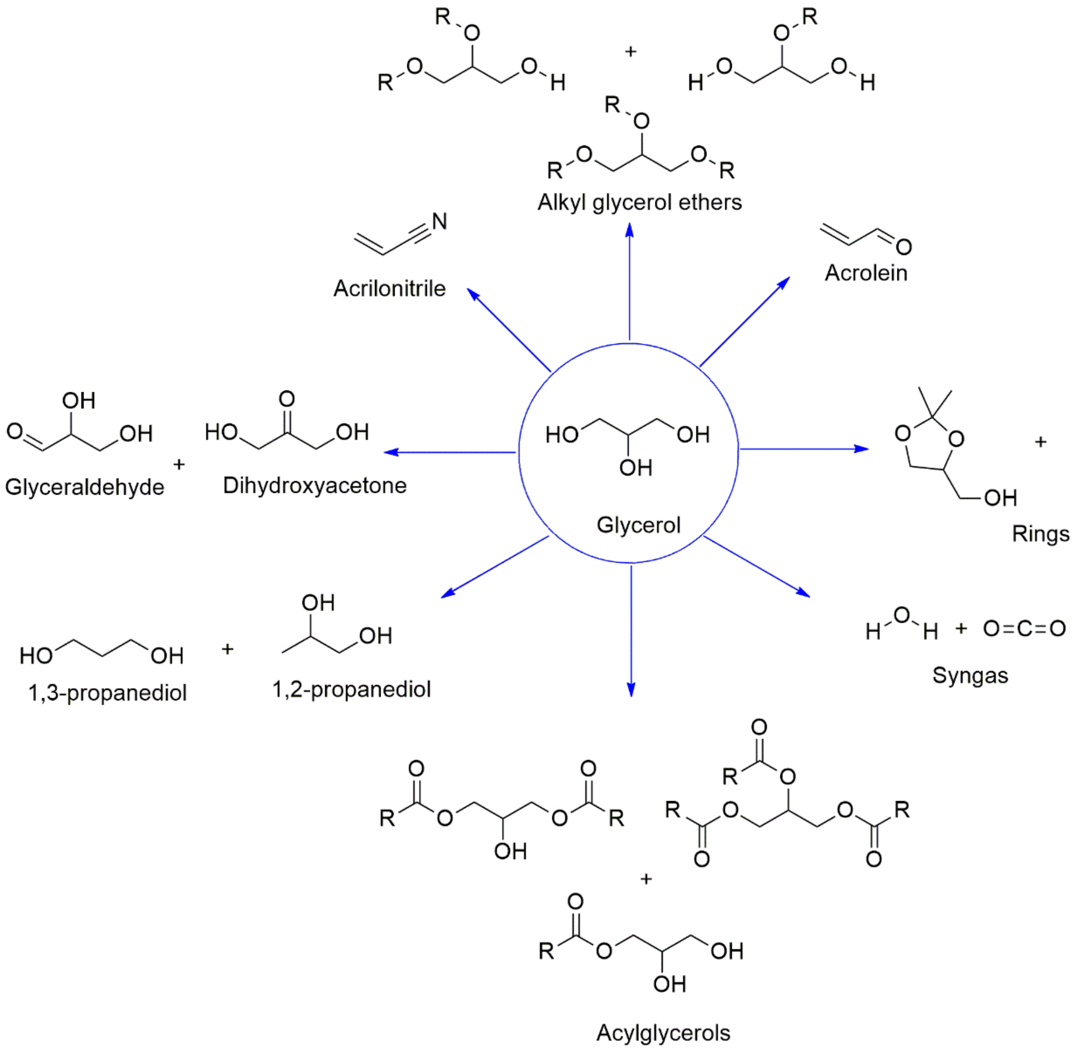

Fig. 4. Glycerol modification routes to obtain various products. *Source: Authors, adapted from* [17] *and* [44].

As aforementioned, glycerol can be transformed into many molecules due to the possibility of functionalization in its three hydroxyls, which are important reactivity points. Among such processes, the transformation of glycerol into ethers is being studied by some authors [17,18,42,45–51].

Glycerol ethers have applications as fuel additives, pharmaceutical intermediates, agrochemicals, solvents and nonionic surfactants. Among these molecules, glyceryl monoethers obtained using C4-C12 aliphatic chain alcohols have been investigated as they can be used as alternatives for petroleum-derived surfactants, as antiseptic and antimicrobial agents, as precursors for polymers and as green solvents. In the case of their interesting features for application, the use of glycerol ethers as a solvent in chemical reactions have attracted great interest currently [26,52–54].

The glycerol alkyl ethers can be naturally occurring with an alkyl or alkenyl chain linked by an ether bound to the glycerol at the C1 position and the remaining two hydroxyls can be free or acetylated. The compounds most known of this class are bathylic, chimylic and selaquilic alcohol, which are found in lipid membranes of marine animals (e.g. whales, starfish, squids and corals). These molecules receive several nomenclatures, such as glycerol ethers, lipid ethers, alkoxyglycerols, among others. They also can have substituents in only one hydroxyl position (monoalkyl ether of glycerol - MAEG), two (DAEG) or in all of their hydroxyls (TAEG) [44,55–57].

The etherification of glycerol to produce its alkyl derivative ethers can be performed via Williamson synthesis in a basic medium, via telomerization with butadiene derivatives, via reduction of compounds, in addition to condensation in an acid medium [53]. When dealing with routes that have a more environmentally friendly appeal, one of the most acceptable is acid condensation because it can use glycerol directly. In another way, other routes could reach a best yield in lower reaction time with higher selectivity, while using toxic and dangerous reactants, for instance in the case of the epichlorohydrin route [58], making it difficult to characterize them as green solvents.

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Some authors have studied the synthesis of glycerol ethers through condensation for several purposes and achieved different selectivities in glycerol mono-, di- and triether by using homogeneous or heterogeneous phase catalysts, as well as the most varied sizes of hydrocarbon chains of alcohols or alkenes for the glycerol functionalization [17,44,55,59,60]. In addition, the alkyl chains of the compounds used in the etherification can be differentiated into linear or branched, long or short, which modifies the characteristics of the resulting ethers that became difficult to predict all the properties of these substances as a solvent, given the infinite possibilities of groups that can be used for the synthesis of the glycerol alkyl ethers. Table 1 shows some studies involving the synthesis of glycerol ethers that have been published.

Among the methods of glycerol alkyl ethers synthesis, the Williamson's route, the reaction with alkenes or the dehydration of alcohols are some frequently used. However, from the green chemistry point of view, a conventional synthesis (via Williamson ethers synthesis) of alkyl glycerol ethers is disliked for generating waste and employing toxic reagents. In this way, despite of the need to improve some issues, the condensation between different alcohols (that can be obtained from renewable sources) could be a better route to produce these compounds. Indeed, glycerol properties can result in low conversions due to its high viscosity and hydrophilicity, or the reproducibility of the conversions are not appropriate when using very hydrophobic organic compounds. In addition, other problems hinder the synthesis of EAG by condensation, such as the low selectivity towards the product of interest, due to the very similar reactivity of glycerol's three hydroxyls, affording the formation of mono, di and triethers mixtures in different proportions.

Glycerol alkyl-ethers are stable in the presence of water and chemically more inert than other glycerol-derived solvents, what make them attractive in the green chemistry concept. So, from the choice of oxygen-linked groups, characteristics with high boiling point, low flash point and volatility can be properties of this solvent. On the other hand, although they have a lower boiling point, for example, greater polarity can be observed in some glycerol alkyl ethers, such as 2,3-trimethoxypropane, 1,3-dimethoxy-2-propanol and 2,3-dimethoxypropan -1-ol, being able to replace polar solvents as dimethoxyethane in reactions [53,58,61,62]. Also, in the case of tunable properties, when trifluoroethanol is used as reactant in the synthesis of ethers, the obtained solvent 1,3-bis (2,2,2-trifluoroethoxy) propan-2-ol can present similar properties to some ionic liquids [63].

The toxicological issues of the glycerol alkyl ethers were evaluated by some studies and, in many cases, the toxicity of these compounds was almost negligible. However, by increasing the size of the hydrophobic part and the number of substituents on the compound, an increase in its toxicity can be observed by some biomodels, such as *Dapnhia magna, Aliivibrio fischeri, Chlamydomonas reinhardtii and Danio rerio* [12,53]. Therefore, several questions must be taken into account for the synthesis of glycerol alkyl ethers in order to obtain a green solvent and their properties deserve more attention as well as the study of the application of them in reaction medium.

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Table 1. Overview of glycerol ethers synthesis via condensation with an alcohol different from glycerol. *Source: Authors.*

Alcohol	***Reference***	***Catalysts and reactants***	***Highlights***
Benzyl	[64]	A-35, Z-Hβ, K-10 montmorillonite, niobic acid and PTSA	MAEG was the main product of the reactions carried out with Hβ (58%) and A-35 (38%). On the other hand, K-10 and PTSA were selective for dibenzyl ethers.
Benzyl	[47]	Sulphated zirconia catalysts	The conversion of benzyl alcohol increased with the reaction temperature and its selectivity decreased with higher MR. Conversions of 80% (30% MAEG, 25% DAEG and 20% TAEG) were achieved with 25 g kg^{-1} of catalyst, 6 h, 1:1 MR.
Butanol	[62]	A-15	Membranes for water removal made it possible to convert 85.1% of glycerol to 82.7% of alkyl ethers of glycerol. The conditions were 160° C, 6 h, 4: 1 MR of butanol: glycerol and 10% A-15.
Butanol	[52]	Hybrid composites from Aquivion-silica	The Aquivion-silica composite exhibited a high catalytic activity (91% *n*-butanol conversion) producing 45% MAEG and 6% dibutyl ether.
Dodecanol	[65]	A-70, CTAB, A-31, A-15, triphyl, hydrobromic, pyrenesulfonic acid, PTSA and 1-bromodecane	Addition of 10 mol% of 1-bromododecane in the reaction medium led to the production of 60% of monododecyl-glycerol ethers. The presence of CTAB was necessary to ensure better contact between the phases.
Dodecanol	[46]	Copolymers of PSt/PSSA (polystyrene/styrene sulfonic acid) and graphite hybrid silica	The heterogeneous phase acid catalysts showed yields of 70% in dodecyl ethers, with MAEG obtaining 16% using MR conditions of 1:4 dodecanol: glycerol, 10% catalyst, 150 °C and 24 h of reaction under vacuum.
Dodecanol	[26]	DBSA, DMSO, sulfolane and 1,4-dioxane solvents	The use of DBSA resulted in the formation of 25% of MAEG in the conditions of 3 h of reaction, 20 mol% of catalyst, 160 °C in a water removal system.
Ethanol	[48]	A-15	The optimized conditions that produced 56% of MAEG were: 238 °C, MR of ethanol: glycerol 16:1 and 0.61 g of catalyst. The temperature, pressure and the amount of catalyst had a statistically significant effect on the MAEG response.

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Alcohol	*Reference*	*Catalysts and reactants*	*Highlights*
Ethanol	[49]	K-10 montmorillonite, H-ZSM-5, Hβ and A-15	Greater conversion (96%) and selectivity (80%) to MAEG were obtained at 180 °C, 3: 1 ethanol: glycerol MR in 4 h with the A-15 acid resin as a catalyst.
Octanol	[66]	USY-550, USY-550-L, USY-650, USY-650-L-2, Hβ e HZSM-5	Hydrophobic zeolites were active in the etherification of glycols and alcohols. The conversion of glycols was closely related to the hydrophobicity index of the material and the structure of the zeolite was crucial for the reaction.
t-butanol	[51]	A-15, A-35, Hβ, Modernite and HY	The Hβ zeolite provided glycerol conversions of approximately 90% for all conditions studied. In the milder reaction conditions of 4 h, 90 °C and 7.6% Hβ, it was possible to convert 96.7% of glycerol with a high selectivity of 81.8% of MAEG.
t-butanol	[67]	A-15, A-35, A-36, A-39, A-31, A-119, HY e Hβ	The most active catalysts in the reaction were A-15 and Hβ. The maximum conversion of glycerol obtained was 96%, at 90° C, MR *t*-butanol: glycerol of 4: 1 and 3 h of reaction. Hβ was the most active catalyst in the reaction, because it produced up to 45% of ethers in 6 h, while Amberlyst led to the formation of only 25% of ethers under the same conditions.

A: Amberlyst, AEG: alkyl ethers of glycerol, CTAB: Cetyl trimethylammonium bromide, DAEG: dialkyl ether of glycerol, DBSA: Dodecylbenzenesulfonic acid, DMSO: Dimethylsulfoxide, Hβ: Zeolite of H-Beta type, HY: Zeolite of H-Y type, MAEG: monoalkyl ether of glycerol, MR: Molar ratio, PTSA: *p*-toluenossulfonic acid, TAEG: trialkyl ether of glycerol.

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Levulinic acid

Levulinic acid (LA) (Fig. 5), also known as 4-oxopentanoic acid or as 3-acetylpropionic acid is a γ-keto acid and non-volatile that has a boiling point of 245 °C. This acid presents great solubility in water as well as in polar solvents, such as diethyl ether and ethanol. The presence of a keto group in its structure make the LA has higher dissociation constants than a common saturated acid, with a pKa of 4.59 (in water at 25 °C). Furthermore, the two functional groups of this compound, carbonyl and carboxyl, afford to it a large variety of application in synthesis, as a consequence, LA together with glycerol were considered by the US Department of Energy's one of the "Top 12" most important bio-based chemicals in the world [68–71]. For instance, LA has potential to be used in the synthesis of several products that nowadays is provided mostly by the petrochemical industry, such as succinic acid, resins, polymers, herbicides, pharmaceuticals, flavoring agents, plasticizers, antifreeze agents, biofuels/oxygenated fuel additives and solvents [72].

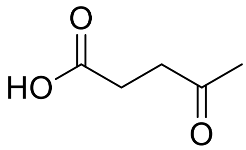

Fig. 5. Chemical structure of levulinic acid. *Source: Authors.*

Currently, the widely known methods of LA production involve the complex conversion of maleic anhydride, the hydrolysis of furfuryl alcohol or the oxidation of ketones with ozone. However, these processes are based on petrochemical and expensive starting feedstocks, which results in the relatively high market price of LA (~US$10 kg^{-1}). In addition, large amounts of side products and residues are produced in these vias. An alternative to reduce the cost of LA production is the conversion of sugars from biomass through acid-catalyzed dehydration and hydrolysis (Fig. 6)[73,74].

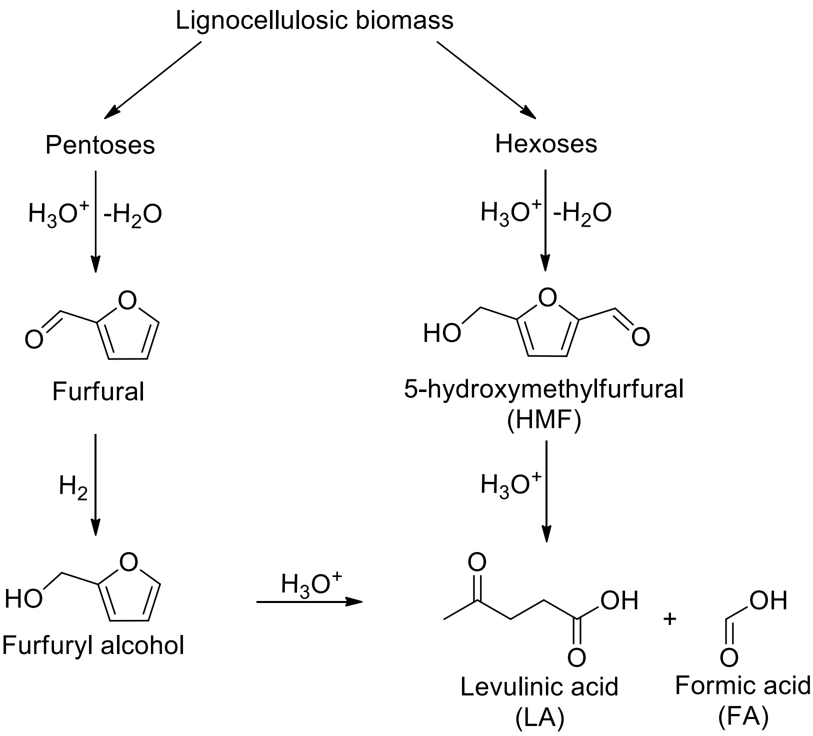

Fig. 6. Conversion of cellulose and hemicellulose into levulinic acid. *Source: Authors, adapted from* [4,75,76].

During the conversion of biomass, in acid medium, the hexose sugars are converted in LA and formic acid (FA), therefore, the maximum theoretical yield possible of LA is 64.5 wt. %. In spite of that, the FA can be used in the production of formaldehyde, rubber, plasticizers, pharmaceuticals and textiles or it can be hydrogen source for other reactions, which is important to the valorization of the whole biomass processing [73,77]. Other factor that affects the LA yield is the instability under acid conditions of the intermediate formed in the biomass conversion, 5-hydroxymethylfurfural (HMF), which can be transformed in other compounds, such as 2,5-furandicarbaldehyde and 2,5-furandicarboxylic acid (FDCA). Also, several reports found side reactions harming the obtaining of LA that led to the formation of black insoluble-materials, called humins. Therefore, the reaction conditions should be optimized in order to increase LA yields [73,74].

A useful tool to improve LA yield and selectivity is the use of solvents in the reaction medium during the conversion of the sugars. The ideal solvent to the reaction mixture would be water, however, side reactions are favored in this medium, such as polymerization and humins formation. Thus, commonly high boiling point solvents are employed, for example, DMSO, *N,N*-dimethylformide (DMF) and sulfolane. These compounds can reduce side reactions, but in contrast, they add to the process energy costs for their separation from the products and to overcome this issue, the reuse of the solvent should be performed [78,79]. For instance, Wang *et al*. [79]reported the use of sulfolane:water mixture as solvent in the conversion of cellulose into LA and recycled three time the organic solvent. In this study, the mass ratio used was of 9:1 (sulfolane:water) and it was achieved 72.5% of LA yield LA (in relation to the total cellulose), even after three solvent recycles. Although the production cost could be reduced, sulfolane is a toxic non-renewable solvent that should be avoided in environmentally friendly processes.

The use of greener solvents was investigated by other authors, such as Han *et al.* [80] that converted cellulose into LA using a solvent derived from biomass, γ-valerolactone (GVL), and the best result obtained was 35.6% of LA yield, at 185 °C in 120 min of reaction by using a lignin-based catalyst. The efficiency of the reaction was related to the ability of GVL to enhance the adsorption of cellulose in the solid catalyst, so the interaction of the substrate with acid sites was more effective. In contrast, at the end of the reaction it was found several by-products such as FA, glucose, furfural and fructose, which indicates that the catalyst promoted the isomerization of glucose into fructose and the selectivity to LA decreases.

Other biomass-derived solvent that was already employed to the conversion of glucose into LA is 2-methyltetrahydrofuran (2-MTHF). Jiang *et al*. [78] investigated the transformation of glucose into LA in water/2-MTHF biphasic solvent system under microwave heating. The selectivity of LA achieved was of 88% with 100% glucose conversion, at 200 ºC by 60 min (pH = 1) using $FeCl_3$ as catalyst. The conversion of Poplar WT 717 in the same conditions gave 53% of LA (based on glucose content in biomass). Despite the less LA production in the biomass conversion, it was demonstrated that 2-MTHF avoided side reaction of C5 and C6 sugar to humins and increases the yields of HMF and LA in relation to the use of water only. On the other hand, 2-MTHF was decomposed into (*Z*)-3-penten-1-ol and 1,4-pentanediol due to acid and high temperatures, wherefore the solvent could not be reused in order to decrease the process costs. By contrast, ionic liquids (ILs), in spite of being expensive, can be more stable at the reaction conditions, so the literature have reported their recycling in some cases of the synthesis of LA [81,82].

In the work of Kumar *et al.* [83], LA selectivity of 56% was attained through glucose conversion, that involved the use of the 1-(4-sulfonic acid)butyl-3-methylimidazolium chloride ionic liquid (IL) (IL-SO_3H) and $NiSO_4$ as catalyst. Besides that, the process cost was diminished, since the IL was recycled three times remaining the LA yields. In another study [82], higher LA selectivity (66%) was achieved from the reaction of cellulose using the IL [C_3SO_3Hmim][HSO_4] under microwave heating. The selectivity was even improved to 86% by the reduction of the mass proportion of 0.55:1:6 to 0.02:1:6 (cellulose: IL: H_2O) and the IL was reused for five cycles by its recovery using methylisobutylketone (MIBK). Surprisingly, the authors found an increase of LA yield from 58% (first cycle) to 66% (fifth cycle), which was attributed to the residual oligomers of cellulose dissolved in the IL. Therefore, the spread of this system to use of lignocellulosic biomass feedstock would be hampered, whereas the high affinity of it toward ILs would make the economical reuse of IL unfeasible as well as the contamination of the products with ILs of unknown toxicity [81].

The disadvantages aforementioned related to the high costs of LA production through different methods could be minimized by the direct use of lignocellulosic biomass, which also contributes to the sustainability of the process by the use of renewable materials [81,84]. For instance, the hydrolysis of cellulosic food waste under microwave irradiation was studied by Chen *et al*. [84], whom achieved 17% of LA yield in only 5 min of reaction in a medium containing water and Amberlyst-36. When DMSO was added to the system, 40% of LA yield was obtained. The authors attributed the efficiency of the reaction to the high content of amorphous cellulose in the raw material and its solubility in DMSO, which affords good interaction between the substrate and the catalyst. The major disadvantage of this system was the coverage of the solid catalyst with the humins formed in the medium that hindered the improvement of LA yields. Moreover, the results attained cannot be reproducible, since the material used is variable due to be an urban waste. Therefore, the use of other biomass sources that could consist by less amorphous cellulose could give lesser LA yields due to biomass recalcitrance [81,85].

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In the study of Kumar *et al.* [85], it was used rice straw as substrate, which is an agriculture residue of known high recalcitrant nature. The approach used to convert the lignocellulosic material into LA was a co-solvent system consisting by dichloromethane (DCM) and HCl that allowed the continuous extraction of furans from reaction medium and made it possible the achievement of 15% of LA yield (57% of theoretical yield), at 180 °C and 3 h. Contrasting the idea of using a residue (rice straw) to avoid environmental issues, the authors applied DCM and HCl, which are hazardous and require recovery and treatment, making the greenness of the overall process dubious. In addition, energy saving was not performed since a high temperature was used. The high temperature (180 °C) was crucial to the LA accumulation, but it reduced the partition coefficient of the products, thus, the conversion of LA required large amounts of solvent, in the volume ratio of 5:1 (DCM:Water). However, fortunately, the system allowed the recovery of 90% of the solvent and its recycling in 5 runs, maintaining the LA yield.

Other authors have reported the LA obtaining by the conversion of acid-pretreated eucalyptus wood. The pretreated material was composed by approximately 63.8% of glucans and 34.6% of lignin. After this stage, LA was obtained by the reaction of the substrate with H_2SO_4 0.2 mol L^{-1} in repeated batch reactions, at 170 °C by 5 h. The study showed that, for the pretreated material, there was need 3 reaction cycles to achieve about 70% of LA yield and for the untreated material the same yield was obtained with 6 batches of reaction [86]. In both investigations [85,86], the issue related to LA recovery was related to the temperature used that led to the formation of humins, which have affinity to water and dragged LA to the aqueous phase. Also, the residual solids (humins and lignin) hindered LA synthesis, not only by physical interaction with it, but also, by reactions between those compounds that were not very well elucidated. Therefore, the production of humins should be avoided to facilitate the LA processing.

When using biomass as substrate for LA synthesis, the pentoses present in the material are easily transformed in humins under the conventional harsh reaction conditions. Although, the reaction conditions used to convert hexoses into LA can transform pentoses into the furfural, which can result in LA too and this procedure involves more reaction steps. To overcome these questions, an alternative could be the pentose extraction prior to the LA production [74].

Runge and Zhang [74] performed a two-stage synthesis of LA from hybrid poplar, which is a material with 14-18% of pentosans. The first step of the process consisted of an acid extraction (1% H_2SO_4), under 160 °C, 60 min, and a 6:1 liquor to wood mass ratio, which removed 85% of pentosans and kept a solid with 92% of hexosans. The second step was the LA production by using the solid material concentrated in hexosans in harsh conditions (190 °C, 5% H_2SO_4, liquor to wood ratio 10:1 and 50 min), which provided 66% of LA yield in a 2L reactor. When using the material non-extracted, under same conditions, the LA yield produced was about 50%. In addition, the furfural obtained from the non-extracted material was very low (<0.1% of theoretical), which confirms that optimal conditions to LA production are too harsh to produce furfural that is further transformed into LA. In short, the process described is quite interesting, however, it aggregates one more stage on biomass conversion that requires time and energy. Additionally, the use of H_2SO_4, a non-recyclable catalyst, results in costs of waste treatment. Therefore, although the common method of LA production by homogeneous acid catalysis usually affords yields up to 70% (in harsh conditions), there are unfeasible steps of separation and treatment of the liquid catalyst, since its distillation is expensive and promotes reactor corrosion. Besides that, side reactions involving humins formation could be also due to the non-selective nature of the homogeneous catalysts [87]. Based on that, it is proposed over the literature the use of heterogeneous catalysts that can be more selective, since there are of possibility of tune its properties, like acidity, porosity and specific area, and they are easily recovered and potentially reused [88–90].

Together with the advantages already mentioned, heterogeneous catalysts reduce the problem of reactor corrosion. However, the use of this type of catalysts, that are generally solids, implies in limited mass transfer, which is worsen depending on the substrate used to LA production. In this context, the conversion of the liquid hydrolysate from *Quercus mongólica* treated with H_2SO_4 towards LA synthesis was investigated by Jeong *et al*. [88], whom showed the efficient use of the commercial solid zeolite Y modified with NaOH as catalyst. The LA production was assigned to the mesopores and strong Lewis acid sites of modified-zeolite. There was demonstrated that the catalyst preferable converts C5 than C6 sugars and it would be suitable for a biorefinery concept, which consists of a multi-step treatment of biomass and uses separated glucose and xylose. However, the maximum LA yield could not be increased, since temperatures higher than 190 °C afforded humin production. Also, a large portion of the C5 sugar remained as furfural and was not transformed in furfuryl alcohol and, then, LA. That was attributed to the insufficient number of strong acid sites in the catalyst and to the glucose or xylose molecules hindering the access of reactant to the active sites. Moreover, no catalyst reuse was investigated, which do not justify the use of a commercial catalyst in the process. Another example of the use of liquid sugar source and a solid catalyst to the production of LA was reported by Kang and Yu [89], whom used sugar beet molasses as substrate and acidic cation exchange resin (Amberlyst-36) as catalyst. The yield of LA achieved was of 53.2% and it was improved to 78% with the removal of non-sugar components from the molasses. In despite of the catalyst be active in a complex substrate (not only composed by C5 or C6 sugars), its reuse was not efficient, since the regeneration required harsh conditions of sulfonation, which resulted in a gradual activity loss.

Solid catalysts have been successful active in transformation of liquid sugar sources, however, many of the challenges associated with them are related to hydrolysis of solid feedstocks, such as biomass and long-chain cellulose. Most of the studies that reports the use solid biomass conversion have showed yields ranging from 30-60%mol of LA in detriment of the use of organic solvents. Furthermore, generally the catalysts used are commercial or of expensive method of production, such as zeolites, ionic exchange resins, zirconium dioxide and Gallium salt of molybdophosphoric acid [83,90,91]. Indeed, it is increasing the development of solid catalysts based on renewable sources for the greener obtaining of LA.

Li *et al.* [92] produced magnetic ferric oxide/SO_4^{2-} biomass-based solid acid from corn straw carbonized and sulfonate (MIO/SO_4^{2-}B-BSACs). Such catalyst was used in the pyrolysis of corn straw and at optimized conditions (250 °C, 70 min) the yield of LA was 23%. The conversion was attributed to the similar structures of corn straw substrate and that of the catalyst that afforded good interaction between them. Meanwhile, the authors did not mention the catalyst lixiviation that could happen, and then the LA yield could be not only from substrate but also from MIO/SO_4^{2-}B-BSACs structure. The magnetic particles of the catalyst enable its separation from reaction medium, which avoids issues related to outgoing in product purification and residues treatment, but still, the use of 250 °C as reaction temperature is an expensive energy input. In lower temperature (185 °C) Han *et al.* [80] attained higher yield of LA (36%) by using a solid catalyst base on alkaline lignin carbonized and treated with a ferrous sulfide solution. The catalyst was used in the synthesis of LA from microcrystalline cellulose in a system of GVL:water as solvent. Those green solvents were used, but the authors did not study the possible recovery and recycling of them, which are expense and environmental effects must be taken into account.

In 2011, Lomba and co-workers studied several thermophysical properties of five compounds classified as green solvents derived from biomass (furfural, furfuryl alcohol, levulinic acid, ethyl levulinate and butyl levulinate). Remarkably, levulinic acid showed low vapor pressure, so it can be considered a suitable candidate for substitution of solvents that are volatile organic compounds (VOCs) and interesting for industrial applications, since its recovery could be facilitated [93].

In relation to the use of LA as solvent, there are reports of it in mixtures to solubilize diesel and in the composition of some degreasing agents. Also, LA and its esters are solvents in polymers, textiles and coatings [93]. Indeed, given LA reactivity, its use to produce other molecules that are widely used as solvents have increasing over the years. Well-known examples of levulinic acid derivative that can be used as solvent are the alkyl levulinates, which will be better explored in the next section of this article.

Alkyl levulinates

Alkyl levulinates (AL) (Fig. 7), particularly those with hydrocarbon chain ranging from C1 to C6, are biomass-derivatives that have valuable properties, such as consistent permittivity, high lubricity, high boiling point, suitable flash point and low vapor pressure. These compounds can be used as building blocks in organic synthesis, as fragrance, as flavoring agents, as well as fuel additives and solvents. Along the properties mentioned, some features make AL more interesting to the use as green solvents, such as adequate cytotoxicity and mutagenicity. Besides that, the possibility of varying the alkyl chain can afford properties tuning to specific solvency requirement [94–96].

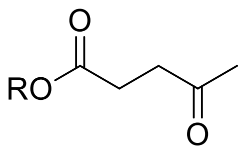

Fig. 7. Chemical structure of alkyl levulinate. *Source: Authors.*

The common routes used to the AL obtaining are direct alcoholysis of carbohydrate biomass (Fig. 8) or conversion of biomass-derived chemical, such as LA, furfuryl alcohol, HMF or furfural. The first report of AL synthesis is over 150 years old, when the authors used LA for the synthesis of methyl and propyl esters, using HCl as catalyst. Ever

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since, the direct esterification of levulinic acid over acidic catalysts or enzymes (lipases) is widely studied and high selectivity values can be attained (up to 99%) [94,95].

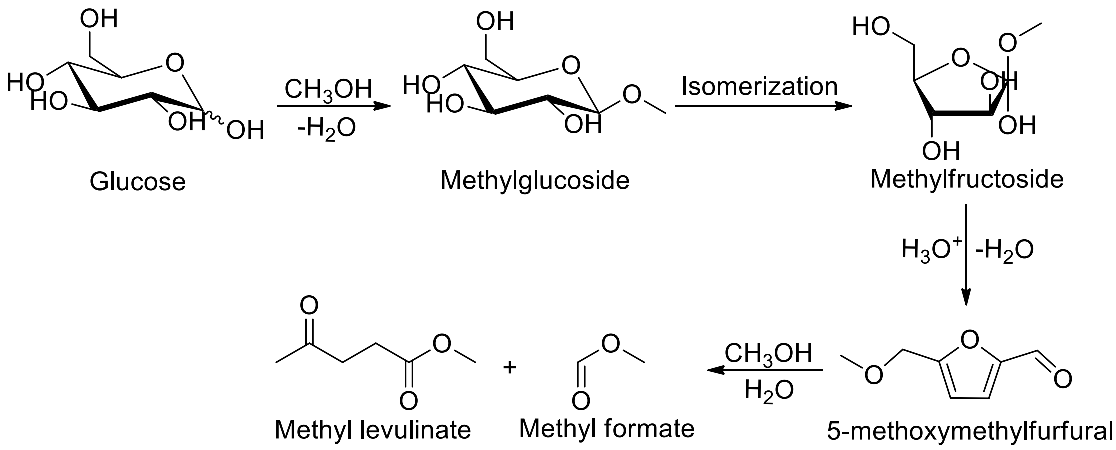

Fig. 8. Proposed reaction pathway for the acid-catalyzed conversion of glucose to methyl levulinate in methanol. *Source: Authors, adapted from* [72].

A great number of studies have reported the production of AL using homogeneous acid catalysts, though some drawbacks, mainly with the rise of the concerns related to environmental issues, have encouraged the use of greener catalyst [69]. For instance, Di *et al*. [97] showed the use of a biocatalyst (lipase), which is used at mild reaction conditions, it is non-toxic, non-corrosive and, in this case, the use of the immobilized enzyme (Novozym 435) gives the advantages of its recovery and reuse. Then, the authors carried out the reaction between LA and methanol in the presence of some solvents, including the 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) IL and the biomass-derived 2-MeTHF, which afforded the yields of 93% and 91%, respectively. The drawback of using 2-MeTHF was the lipase deactivation under sequential uses, since in 5 cycles the LA yield decreased to only 19.1%, while in [bmim][PF_6] it reached to 43.2%, which limits the dilution of the high cost of enzymatic process. Additionally, the process lasted 24 h, being too long in relation to the conventional homogeneously catalyzed (up to 6 h).
The alternative use of chemical heterogeneous catalysts was reported, such as the commercial heteropolyacids, sulfated metal oxides, zeolite molecular sieves and hydrotalcite-like compounds [69], whose also present the disadvantage of high cost. Recently, Bosilj *et al.* [98] reported the use of a cheaper biomass-derived catalyst in the conversion of glucose into ethyl levulinate (EL). In this study, an acid-functionalized hydrothermal catalyst derived from glucose was produced by hydrothermal carbonization of glucose that was first treated with sodium borate (borax) to generate carbon nanoparticle size and, then, it was sulfonated with H_2SO_4. By using this material and ecofriendly solvents (ethanol, glycerol and GVL), the EL yields attained were as high as 25-37 mol%, depending on the solvent system used. In 6 h of reaction at 200 °C, the yields achieved were of 37, 35 and 25 mol% of EL, when using ethanol:glycerol, etanol:GVL and etanol by itself as a solvent, respectively. One inconvenience of using GVL is its probable dehydration to α-angelica lactone and hydration to levulinic acid, which could further form EL with ethanol, giving an EL yield that account not only to the original substrate used (glucose). On the other hand, the use of glycerol was advantageous, since it promoted rapidly conversion of glucose into 5-HMF and reduced humin deposition on the reactor wall.
Yang *et al*. [99] prepared a magnetic carbonaceous solid acid (SMWP) catalyst from waste paper scraps via Fe-impregnation, carbonization and sulfonation process, which could easily be recovered from reaction medium with external magnetic fields. The SMWP catalyzed the alcoholysis of furfuryl alcohol with *n*-butanol, reaching to 90.6% yield of *n*-butyllevulinate in 5 h at 120 °C, such catalytic activity was assigned to a strong acidity and the affinity towards furfuryl alcohol, due to the presence of the SO_3H, COOH and phenolic OH groups on the catalyst surface. Moreover, the catalyst was reused for 7 times with a slightly loss of activity that was attributed to the adsorption of some oligomeric by-products on the surface of SMWP.
The results aforementioned are quite interesting from the synthetic point of view, however, it was reported the use of pure substrates (furfuryl alcohol and glucose) that are costly products. Therefore, the investigation of the direct synthesis of alkyl levulinates from lignocellulosic materials have increased, since the reaction can be performed in a one-step way, which reduces stages of products purification and the amounts of wastewater, besides that, this method could save time and be cost effective [69,94,95]. On the other hand, recalcitrance and

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insolubility of the raw biomass require drastic reaction conditions for the alcoholysis/hydrolysis of the structural carbohydrates, which hinders the obtaining of alkyl levulinates selectively with the yields obtained about 10–30% [100]. Therefore, some authors described the fractionation of the lignocellulosic material prior to its conversion into AL. For instance, Liang *et al*. [101] carried out the preparation of bifunctional solid-acid catalyst from the hydrothermal hydrolysate of dewaxed wood powder of *eucalyptus globulus* residue that was sulfonated and impregnated with Zr^{4+}. The other portion of the biomass hydrolyzed had the lignin removed with DES and, then, it was used as substrate to the production of methyl levulinate (ML) and the highest yield reached was 38.7%. This study showed the improvement of the ML yields by using a pretreated lignocellulosic material. Nevertheless, the proposal is a multistage process, which can result in exceeding steps of recovery and residues treatment.

The one-pot synthesis of methyl levulinates was carried out by Feng *et al.* [100] by using bamboo as carbohydrate source, the ML yields achieved were up to 48.7%, in a solvent system of dimethoxymethane/methanol, at 200 °C for 150 min. The authors attributed the result to the ability of dimethoxymethane to act as an electrophile that promoted the transformation of furfural to 5-hydroxymethylfurfural and rapidly conversion to ML and to the methanol act as solvent/reactant that dissolved the reaction intermediate, avoiding furans polymerization and promoting continuous liquefaction of the material and releasing of ML. In another study, Guan *et al.* [102] used IL as catalyst to produce ethyl levulinate from wheat straw in a one-pot reaction in ethanol. In this case, IL and ethanol also played the role of solvent and the highest biomass conversion, 85.5%, was obtained in 1 h at 200 °C by using the IL [HSO_3-BMIM][HSO_4]. The overall EL yield attained was 16.2% and it was the main component in the liquid products, since its content was 28.1%.

The use of solid catalyst is very limited in the processes of direct biomass conversion, thus, ILs seems to be a good option, since they can increase the dissolution of lignocellulosic materials and act as catalysts in the alcoholysis of the substrates. Therefore, the recovery and the reuse of ILs should be optimized to the reduction of processes costs. Also, one-pot reaction is advantageous in relation to biomass fractionation, because it reduces process steps. Some authors have highlighted that direct obtaining of alkyl levulinates instead of levulinic acid is advantageous, because the levulinate esters, mainly those of short chain (C1-C4), present lower viscosity, acidity and boiling point. Additionally, ALs are non-corrosive and more stable under reaction conditions, which requires lower energy consumption in the stage of their separation from the medium. One issue in the one-pot reaction may be the low selectivity achieved of AL, but, in comparison to dehydration/hydration reaction to obtain biomass derivatives and further convert them into AL, reactions of biomass performed directly in alcohols can protect highly reactive intermediates and prevent unwanted polymerization reactions, improving the yields of the required products [69,100,102].

About the potential use of AL as solvents, The group of Sah and that of Schuette published some physical and chemical properties of methyl to hexyl levulinates, whose had boiling point in the range of 190−270 °C, they were all soluble in classical solvents (e.g., alcohols, ethers and chloroform), but insoluble in water (except methyl levulinate) [103,104]. Lomba *et al.* [93] measured the vapor pressures of alkyl levulinates and the values obtained at 100 °C were 5.96, 4.69, and 1.56 kPa for methyl, ethyl and butyl levulinate, respectively. These results show their easily handle in relation to chlorinated solvents that present vapor pressures more than 400 kPa at the same temperature. Other property evaluated was the partition coefficient in octanol:water (Log P) that showed the highest solubility in water of ML among the esters, whose water solubility decreased as the alkyl chain increased. It is important, because the solubility in water affects the potential for biodegradation of the compounds. In addition, Ferrer *et al* [105] presented in their patent of the use of alkyl levulinates for metallic surface degreasing some data showing that butyl, iso-butyl and pentyl levulinates present excellent environment, health and safety properties, such as not being cytotoxic neither mutagenic.

Marcel *et al.* [96] performed the use of alkyl levulinates (methyl, ethyl and *n*-butyl) as solvents for the heterogeneously Pd-catalyzed Heck coupling, as far as it is known, for the first time. The reaction of Heck coupling between 2-iodoanisole and *n*-butylacrylate giving 2-methoxycinnamic acid butyl ester using alkyl levulinates as solvents showed yields ranging from 88 to 98%. The efficiency of the process was attributed to the catalysis occurring through the soluble Pd species, since, those species leach from the support and form complexes with reactants/solvents in solution and, after, Pd is redeposited on the support. Methyl and ethyl levulinates afforded 96% and 98% of product yields, while in *n*-butyl levulinate the yield was 88%, however, the non-solubility in water of n-butyl levulinate is an advantage for its recovery and treatment before environmental disposure. This solvent was then used in the reactions of other aryl halides, taking to conversions between 83 and 100%. These results were different from that usually observed for C-C couplings, when normally lower yields are attained for deactivated aryl halides, including iodides, which was attributed to a specific interaction between the solvent and the catalyst under the conditions, due to different degrees of reduction of Pd species. Additionally, *n*-butyl

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levulinate was recovered by simple distillation and its integrity was asserted by NMR. Afterwards, *n*-butyl levulinate was reused in one run that presented the same result of the first. More studies are need to fully explain the reactivity improvement in AL. Besides that, these compounds revealed potential that should be explored in other reaction. With respect to the reliable of the use of alkyl levulinates as green solvents it also requires further investigation towards their toxicity.

γ-Valerolactone (GVL)

γ-Valerolactone (GVL) has attracted great attention in the last years especially due to its exceptional chemical and physical properties, such as low melting (-31 °C) and high boiling (207 °C) points, remarkably low vapor pressure even at higher temperatures (3.5 kPa at 80 °C), miscibility with water without azeotrope formation, no peroxides formation in the presence of air and high stability at neutral pH, making it a safe material for large-scale use [1,106]. The chemical structure of GVL is shown in Fig. 9.

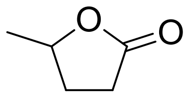

Fig. 9. Chemical structure of γ-valerolactone (GVL). *Source: Authors.*

Owing to the aforementioned properties, GVL is seen as a renewable solvent and as a potential biofuel additive. For instance, Strappaveccia *et al.* [107] identified GVL as a sustainable alternative to classic and toxic dipolar aprotic solvents, such as acetonitrile, dimethylformamide (DMF), or *N,N*-dimethylacetamide (DMA) in cross-coupling reactions. The authors observed a successful clean use of GVL in palladium-catalyzed Heck reaction of several small molecules (iodobenzene with acrylic esters and iodobenzene with styrenes). Horvath *et al.* [106] carried out a comparative evaluation of GVL and ethanol as fuel additives by mixing 10% (v v^{-1}) GVL or ethanol with 90% (v v^{-1}) 95-octane gasoline. The results showed that most of the data for GVL are comparable with ethanol and its lower vapor pressure leads to improved combustion at similar octane numbers. Besides that, GVL can also be precursor to high-grade liquid alkene transportation fuels and fine chemicals, including 2-methyltetrahydrofuran (2-MTHF), 1,4 pentanediol, alkyl pentenoates and α-methylene-γ-valerolactone, which may find application in the production of biobased polymers [106,108–113]. Nevertheless, the maximum economic and environmental benefits associated with utilization of GVL will only be achieved if a greener process is employed during its production [112].

The synthesis of GVL can follow two different pathways that entail in a sequence of dehydrogenation/hydrogenation of LA or vice versa (Fig. 10). The first pathway is a catalytic hydrogenation of LA to yield 4-hydroxypentanoic acid, followed by acid-catalyzed intramolecular esterification to form GVL. The second pathway is an endothermic acid-catalyzed dehydration of LA to angelica lactones and under H_2 atmospheres, the preferred lactone GVL is thermodynamically obtained. Depending on the reaction conditions such as solvent, metal catalyst and presence of residual acid-impurities, one pathway may be favored [114]. Abdelrahman *et al.* [108] observed that Ru-catalyzed LA hydrogenation in the aqueous phase at temperatures below 150 °C, it forms exclusively via intramolecular esterification of 4-hydroxypentanoic acid. It is also important to highlight that two hydrogen sources are possible, molecular hydrogen (H_2) or catalytic transfer hydrogenation using alcohols or formic acid [77,115–117].

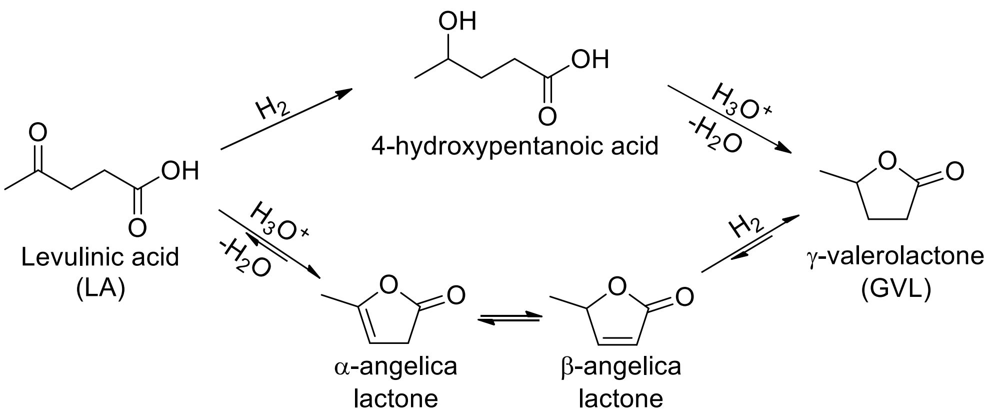

Fig. 10. Synthesis of GVL from LA. *Source: Authors, adapted from* [4,108,114].

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Heterogeneous catalysis may provide an efficient methodology for LA conversion allowing high reaction rates and high selectivity of the target products. The ability of a range of precious metals to catalyze LA hydrogenation has already been extensively explored, with good GVL yields (in the range of 80 to 99%) obtained from ruthenium-supported catalysts [108,116,117]. For instance, Al-Shaal *et al.* [112] examined the ability of Ru/C to catalyze LA hydrogenation using 12 bar H_2 in methanol, ethanol and 1-butanol at 130 °C for 160 min. Among the alcohols screened, methanol facilitated the highest GVL yield, 84.4%, while ethanol and 1-butanol resulted in yields of 61.1% and 39.7%, respectively. When mixtures comprised of water (10% v v^{-1}) and a given alcohol (90% v v^{-1}), were utilized as solvents, ethanol/water and 1-butanol/water systems resulted in a substantial increase in GVL yields. The result can be explained by the lower H_2 solubility in less polar alcohols [118] and the high capacity of water to dissolve H_2 [119]. In fact, the authors obtained 86.2% yield of GVL using only water as a reaction solvent in the LA hydrogenation. This is very important because the commercial LA production via hydrolysis of lignocellulosic biomass is generally performed in water-contained medium that results in LA product streams containing water [110], which facilitates closer process integration and increasing efficiency, by removing the costly need to separate water from LA feeds prior to hydrogenation. However, the presence of water in LA product streams could create additional challenges with regard to catalyst stability. When alcohols are employed as reaction solvents, both LA and GVL can undergo esterification. Thus, Al-Shaal *et al*. [112] also showed the hydrogenation of alkyl-levulinates (methyl-levulinate and butyl-levulinate) in methanol, using identical conditions to those employed for LA (12 bar H_2, at 130 °C for 160 min). GVL yields were similar to those obtained from LA, establishing that esters of LA can be readily hydrogenated to GVL as well. The conversion of lignocellulosic biomass to levulinic esters instead of LA could enables higher yields and easier product separation [87], suggesting an alternative route to GVL synthesis.

To achieve an economical and sustainable production of GVL, the development of noble metal-free heterogeneous catalysts is an important research target, as noble metal-based catalysts are costly. An effective non-noble-metal catalyst was studied by Shimizu *et al.* [120]. The hydrogenation of LA to GVL under solvent-free conditions in 8 bar H_2 at 140 °C for 5 h in the presence of 1 mol% of Ni-MoOx/C catalyst resulted in 97% yield. However, the catalyst recyclability was lower, achieving only 50% yield of GLV after the first cycle. Yi *et al.* [121] carried out a comparative study using Ni and Ru catalyst, both supported on HZSM-5, at 220 °C for 10 h in 30 bar H_2 and using 1,4-dioxane as solvent. The catalytic experimental results showed that Ni/HZSM-5 catalyst achieved 93.1% yield of GVL, while Ru/HZSM-5 catalyst exhibited 85.7% yield of pentanoic esters (PE) and pentanoic acid (PA) under identical conditions (Fig. 11). Therefore, it was found that Ru/HZSM-5 increased the strong acidic sites and provided the ring opening of GVL, promoting the formation of PE and PA. In comparison, Ni/HZSM-5 catalyst was much more effective to produce GVL, once it showed relative lower acidic sites and negligible GVL ring-opening ability.

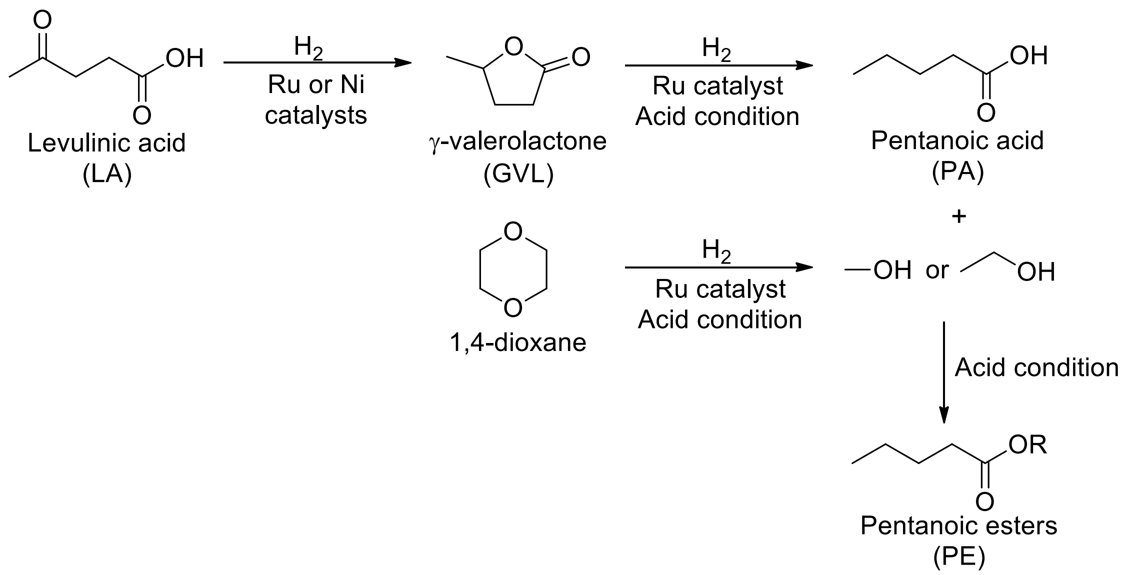

Fig. 11. Proposed reaction pathway during the hydrogenation of LA over Ni/HZSM-5 or Ru/HZSM-5 catalysts in 1,4-dioxane solvent. *Source: Authors, adapted from* [121].

A greener process to convert LA to GVL was proposed by Liu *et al.* [122], which used a cobalt-based catalytic system in order to avoid the use of noble metal catalysts. The highly efficient catalytic system was composed of commercially available cobalt salt, $Co(BF_4)_2{\cdot}6H_2O$ and a tetradentate phosphine ligand $P(CH_2CH_2PPh_2)_3$, affording 95% GVL yield at 100 °C and with atmospheric H_2 pressure. Cobalt was also used as catalyst for GVL synthesis by Murugesan *et al.* [123], which applied LA for the preparation of cobalt-based nanocatalysts. These nanoparticles created reusable catalysts (up to 4 times) for the hydrogenation of LA, achieving 97% GVL yield in the following reaction conditions: 30 bar H_2, 1,4-dioxane as solvent, 120 °C during 24 h.

Another approach to produce GVL is using a one-step conversion of carbohydrates. Both Brønsted acid catalyst and hydrogenation catalyst are required for the conversion of carbohydrates into GVL in the one-step method [124,125]. The acidity of Brønsted acid catalysts is determined by its dissociation constant (pKa), but also dependent on the solvent. Particularly water-contained solvents that are common in the biomass conversion process, usually negatively affect the acidity of Brønsted acid catalysts [126]. Cui *et al*. [109] studied several carbohydrates conversion into GVL combining a strong Brønsted acid, $H_3PW_{12}O_{40}$ and Ru/TiO_2 catalysts. The one-step conversion in a monophasic γ-butyrolactone/water (80/20, v v^{-1}) solvent under a mild reaction condition (150 °C and 40 bar H_2) resulted in GVL yields of 70.5 and 58.5 mol% from inulin and sucrose, respectively. As the most abundant biomass, cellulose is considered as an ideal resource to produce GVL. However, a direct conversion of cellulose into GVL is more challenging due its recalcitrance structure. The direct conversion of cellulose to GVL was investigated by the authors using the same conditions above and a yield of 40.5% of GVL was obtained.

Most works concerning GVL production from carbohydrates involves the selective dehydration of carbohydrates to LA followed by hydrogenation of LA to give GVL by using an external H_2 supply. A different route to convert carbohydrates into GVL without use of any external H_2 supply was reported by Deng *et al.* [77]. The authors related a hydrogenation process using ruthenium-based catalytic systems accomplished only in the presence of the formic acid produced from the original acidic dehydration step of glucose. The route improved the atom economy of the process and avoided the energy-costly separation of LA from the mixture of LA and formic acid in aqueous solution. However, it is important to note that the proposed process presents some drawbacks, such as temperatures as high as 220 °C and reagents that are corrosive and toxic (hydrochloric acid and pyridine). Son *et al*. [117] synthesized GVL from one-pot dehydration/hydrogenation reaction of fructose in water solvent over supported metal catalysts. In this reaction, formic acid played two roles, an acid catalyst for dehydration of fructose to LA, and a hydrogen source for hydrogenation of the obtained LA. The Au/ZrO_2 was the best catalyst showing an overall GVL yield of 48% and could be reused for several times, though it was partly deactivated. On the other hand, Fabos *et al*. [116] showed the hydrogenation of LA to produce GVL with a small excess of formic acid in the presence of the ruthenium Shvo catalysts. The reactions were performed at 100 °C in an open vessel with yields higher than 99% after 5 h. The only byproducts were water and carbon dioxide, which were easily eliminated, by distillation in the case of water and the carbon dioxide was bubble out of the solution.

Although the transformation of LA to GVL can be achieved using heterogeneous catalysis, homogeneous catalytic systems that operate under milder reaction conditions give higher selectivities and can be recycled continuously. By using ruthenium complexes with a related chelating triphosphine ligand, N-triphos ($N(CH_2PPh_2)_3$), Phanopoulos *et al*. [127] obtained high yields of GVL (77-95%) by using [RuH_2(CO)(N-triphos)] as catalyst with either NH_4PF_6 or *para*-toluenesulfonic acid additives under the following conditions, 160 °C and 65 bar H_2. A range of palladium complexes as catalysts was proved to be effective for the GVL synthesis under transfer hydrogenation using formic acid as hydrogen source and carrying out the reaction at only 5 bar H_2 at 80 °C for 5 h [128]. The best-performing catalyst [Pd(DTBPE)Cl_2] (DTBPE=1,2-(bis-di-tert-butylphosphino)-ethane) displayed 98% GVL yield. In addition, the catalyst could be recycled several times, but showed loss of catalytic activity due to the in-situ formation of an inactive Pd-carbonyl and a Pd-hydride dimer complex. Nevertheless, this report demonstrates the first use of Pd complexes for these transformations under mild reaction conditions [128].

GVL is a promising building block in organic synthesis due to its functional groups and reactivity. Although it contains a chiral center, it is usually produced and used in the racemic form because major applications, such as fuels or solvents, do not require one specific enantiomer. However, enantiomeric purity is important in the fragrance, flavoring and pharmaceutical industries, where a specific enantiomer can present different properties [129,130].

Starodubtseva *et al*. [131] studied the conversion of LA and γ-ketoesters derived from LA to enantiopure lactones using homogeneous catalysis. LA could be converted to (*S*)-GVL in moderate yields of 66% with 98.5% *ee* after 5 h at 60 °C and 60 bar H_2 in ethanol using a Ru-BINAP catalysts prepared in situ and activated with HCl. When ethyl levulinate was used as substrate in the same reaction conditions, 95% yield and 99% *ee* for (*S*)-GVL was

obtained. Using $RuCl_3$–BINAP–HCl catalytic system, 96% (*R*)-GVL yield and 99% *ee* was achieved from methyl levulinate under similar catalytic conditions [132].
Biotransformations can also address the enantiomeric purity request, showing the benefit of mild reaction conditions and remarkable chemo-, regio-, and stereoselectivity. Gotz *et al.* [111] presented a chemo-enzymatic reaction sequence for the synthesis of optically pure (*S*)-GVL (Fig. 12). Initially, LA was esterified with ethanol at 70 °C for 16 h in the presence of Amberlyst 15 and $MgSO_4$, resulting in 95% yield of ethyl levulinate. Without further purification, isolated ethyl levulinate was reduced by (*S*)-specific carbonyl reductase from *Candida parapsilosis* (CPCR2) at 30 °C and using isopropanol as co-substrate to produce (*S*)-ethyl-4-hydroxypentanoate (95% of conversion and >99% *ee*). A subsequent lactonization of (*S*)-ethyl-4-hydroxypentanoate catalyzed by immobilized CalB yielded the desired (*S*)-GVL (>99% ee) at a reaction temperature of 30 °C. The heterogeneous catalyst was easily filtered off, and no further downstream processing was needed. An overall yield of approximately 90% (*S*)-GVL (based on LA) was achieved in this chemo-enzymatic reaction sequence.

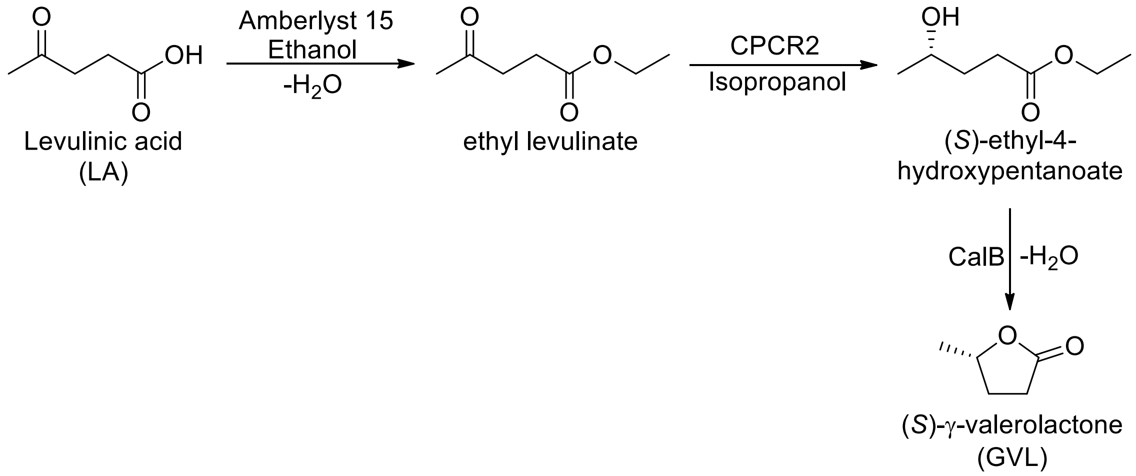

Fig. 12. Chemo-enzymatic route for the synthesis of enantiomerically pure (*S*)-GVL.
Source: Authors, adapted from [111].

2-Methyltetrahydrofuran (2-MTHF)

2-Methyltetrahydrofuran (2-MTHF) may find use as a fuel and a green alternative solvent to tetrahydrofuran (THF) with favorable physical and chemical characteristics, such as higher boiling (80.2 °C) e lower melting (-136.0 °C) points, higher stability, lower volatility and water immiscibility [7,76,129,133]. The chemical structure of 2-MTHF is shown in Fig. 13.

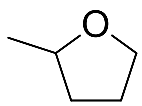

Fig. 13. Chemical structure of 2-methyltetrahydrofuran (2-MTHF). *Source: Authors.*

Because of the low melting point and low viscosity (1.85 cp at -70 °C), 2-MTHF is increasingly used in organometallic reactions, such as Grignard reaction, low-temperature lithiation, lithium aluminum hydride reductions, Reformatsky reaction and metal-catalyzed coupling reactions [7]. For instance, Mondal and Mora [134] related a catalyzed Suzuki–Miyaura cross-coupling reaction of acid chlorides and aryl boronic acids to yield aryl ketones using 2-MTHF as solvent. The great benefit of the water-immiscible 2-MTHF use was the easy isolation of the crude reaction mixture just by separation of 2-MTHF and water layers, followed by the evaporation of 2-MTHF. Also, it is important to highlight that 2-MTHF performed better than acetone, toluene, DMF, THF, acetonitrile, dichloromethane, PEG-400, isopropanol and a 3:1 mix of 2-MTHF and water. The 2-MTHF use in chemical reactions have been extensively reviewed elsewhere [8,133,135]. Besides that, Antonucci *et al.* [136] revealed that 2-MTHF has low toxicity and with a maximum concentration of 2% would not be expected to contribute to any toxicity potentially exhibited by an active pharmaceutical ingredient containing this solvent, and that is why, it has been approved for use in pharmaceutical chemical processes.
The synthesis of 2-MTHF from GVL involves a hydrogenation of the carbonyl group to yield the cyclic hemiacetal

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(5-methyltetrahydrofuran-2-ol), which is in equilibrium with the 4-hydroxylpentanal. Further reduction of the remaining carbonyl group affords 1,4-pentanediol and an acid-catalyzed dehydration leads to cyclization of the diol by etherification to form 2-MTHF (Fig. 14) [2]. Thermodynamic data showed that the GVL ring-opening to 1,4-pentanediol is a highly endothermic process at 250 °C ($\Delta G^0 = 70$ kJ mol^{-1}) [137]. Therefore, harsher reaction conditions are needed to obtain 1,4-pentanediol and consequently, 2-MTHF from GVL, making the process more challenging when compared with the GVL synthesis from LA [114].

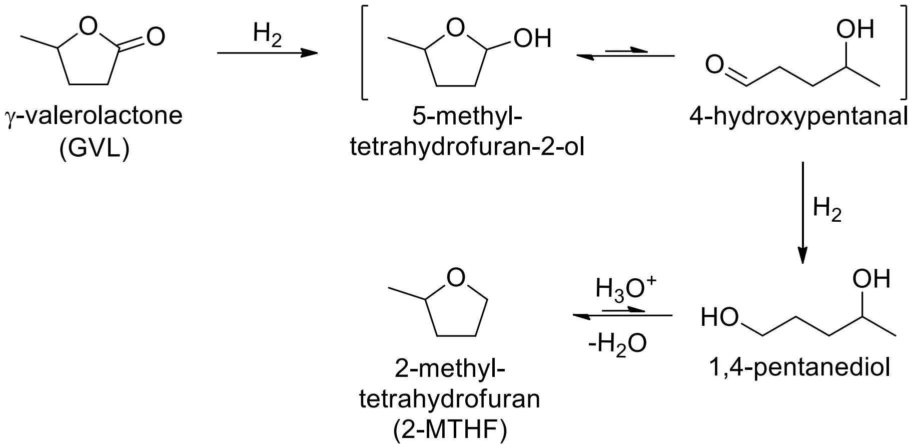

Fig. 14. Synthesis of 2-MTHF from GVL. *Source: Authors, adapted from* [2,114].

The production of 2-MTHF based on GVL as a substrate was investigated by Al-Shaal *et al*. [76] applying Ru/C as catalyst. A full conversion of GVL was obtained in a solvent-free reaction system after 24 h at 190 °C and using a H_2 pressure of 100 bar with a maximum 2-MTHF yield of 43%. The hydrogenation of GVL to 2-MTHF was coupled with the formation of by-products such as 2-butanol, butane, 1,4-pentanediol, 2-pentanol, 1-pentanol, pentane and methane (Fig. 15). On the other hand, Zhang *et al*. [138] using Ni-MoOx/Al_2O_3 as catalyst found, in addition to the 1,4-pentanediol, others by-products such as pentenoic and valeric acids. The maximum 2-MTHF yield (31%) was achieved when the reaction conditions were 200 °C, 40 bar H_2 during 4 h. It is important to highlight that 1,4-pentanediol yield was 68% in this same reaction condition. Du *et al.* [113] have demonstrated that tuning the acidic properties of the catalyst surface alternates the product distribution in the hydrogenation of GVL. The catalyst Cu/ZrO_2 was significantly modified by calcination in air at different temperatures in the range of 300–700 °C for 4 h. It was found that the catalyst obtained by 400 °C-calcination can deliver a remarkable 2-MTHF yield as high as 91% within 6 h of reaction, using ethanol as solvent and 60 bar H_2 at 240 °C. However, the same catalyst calcinated at 600 °C resulted in 1,4-pentanediol as the major product (73% yield), while 2-MTHF yield was only 20%.

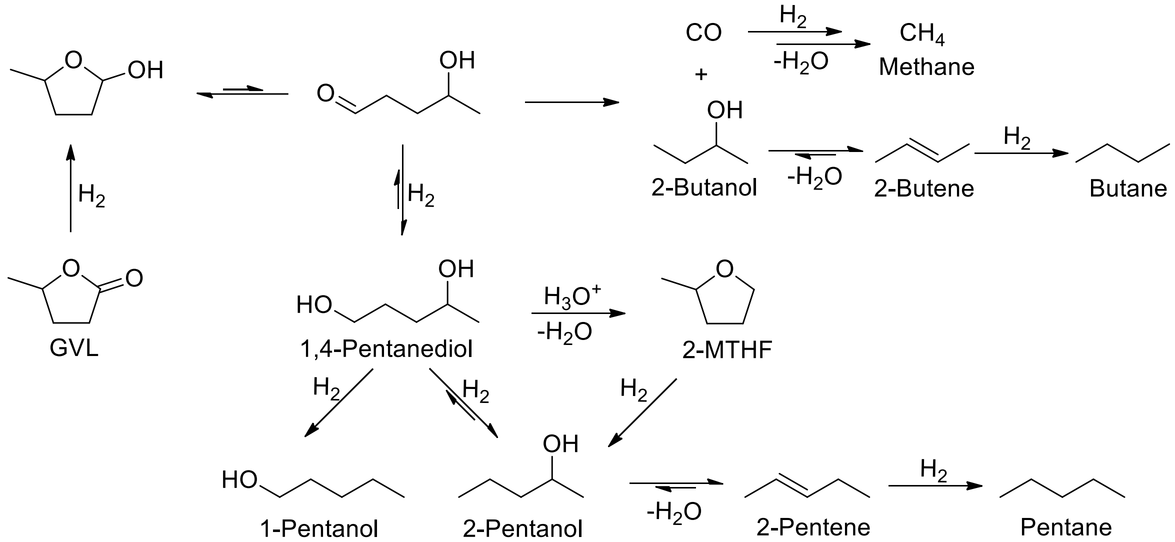

Fig. 15. Proposed reaction pathway for the formation of by-products during the synthesis of 2-MTHF from GVL over Ru/C catalyst. *Source: Authors, adapted from* [76].

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A direct conversion of LA to 2-MTHF involves several reaction steps, including hydrogenation of LA into GVL; further ring-opening to 1,4-pentanediol and final dehydration to afford 2-MTHF. Al-Shaal *et al*. [76] using a two-step hydrogenation reaction over Ru/C produced 2-MTHF from LA. The first hydrogenation step, LA was totally converted to GVL under 12 bar H_2 at 190 °C and 45 min [112]. At the end of this step, the formed water was evaporated from the reaction mixture and the catalyst was collected, washed, and dried. This procedure was necessary because water resulting from the hydrogenation of LA may inhibit the later dehydration reaction of 1,4-pantanediol to 2-MTHF. Thus, the second hydrogenation step was conducted using the dried catalyst and the produced GVL applying 100 bar H_2 at 190 °C. After 4 h of reaction, 90% conversion of GVL and 61% yield of 2-MTHF was obtained.

Novodárszki *et al*. [139] studied the solvent-free conversion of LA to 2-MTHF over Co/silica catalysts by applying a flow-through fixed-bed microreactor. At 200 °C and 30 bar H_2 total pressure in the steady state, GVL was obtained with 98% yield at full LA conversion. In addition, at temperatures higher than 225 °C, the hydrogenation activity was high enough to cleave the GVL ring and obtain 2-MTHF with 70% yield. On the other hand, Xie *et al.* [140] showed that a bimetallic Cu-Ni/Al_2O_3-ZrO_2 catalysts can selectively hydrogenate LA to 2-MTHF using 30 bar H_2 at 220 °C and 10 h of reaction. It was demonstrated that both Cu:Ni and Al:Zr ratios affected the selectivity to 2-MTHF significantly. The bimetallic catalysts containing 10 wt.% Ni and 10 wt.% Cu resulted in 99.8% of 2-MTHF selectivity at full conversion of LA, when the Al:Zr ratio was 9:1. The outstanding catalytic performance of the catalyst was related to its mesoporous structure, the acidic properties of the support and the synergistic effect between Cu and Ni. It is also important to note that the catalyst could be reused five times without a considerable loss of catalytic activity and selectivity.

The important role of the solvent is highlighted by several studies. As aforementioned, the transformation of GVL into 2-MTHF is reported to be strongly inhibited by water [75]. Obregon *et al.* [141] proved that 2-MTHF yield significantly improves if alcohols are used as solvents instead of water. The authors carried out the one-pot hydrogenation of LA to 2-MTHF using non-noble metal catalysts (Ni-Cu/Al_2O_3) in water, ethanol, 1-butanol and 2-propanol. The catalysis with Ni/Al_2O_3 (35 wt.% Ni loading) was dependent on the solvent, being observed the best 2-MTHF yield of 45.9% using the 2-propanol in the following conditions: 250 °C, 70 bar H_2 and 5 h. Meanwhile, Cu/Al_2O_3 catalyst (35 wt.% Cu loading) with the same solvent resulted in 75% 2-MTHF yield in the following conditions: 250 °C, 70 bar H_2 and 24 h. Besides that, synergistic effects were observed when bimetallic Ni-Cu/Al_2O_3 catalysts were used, reaching to 56% 2-MTHF yield in 5 h at 250 °C for the optimum Ni/Cu ratio (23 wt.% Ni loading and 12 wt.% Cu loading).

The role of the hydrogen source on the selective production of GVL and 2-MTHF from LA was investigated by Obregon *et al.* [114] using three different solvents (1,4-dioxane, 1-butanol and 2-propanol) under reactive H_2 and inert N_2 atmospheres. The applied reaction conditions (250 °C, 40 bar H_2 initial pressure and 5 h reaction time) were combined with the use of the following catalysts: Ru/C, Ni/Al_2O_3 and Ni-Cu/Al_2O_3. Under N_2 atmosphere, catalytic transfer hydrogenation reactions are the principal source of hydrogen for the transformation of LA into GVL or 2-MTHF. Low hydrogen availability provided by a poor hydrogen donor such as 1,4-dioxane resulted in relatively low LA conversions for the three tested catalysts. The performance of all the three catalysts was improved with 2-propanol as the solvent, which is a well-known hydrogen donor [142], achieving more than 70% GVL yield. However, these in situ-generated hydrogen sources alone were insufficient to convert the highly stable GVL into 2-MTHF (yields were lower than 3%). Under a H_2 atmosphere, catalytic transfer hydrogenation and hydrogenation with molecular H_2 were effective and very fast at producing high yields of GVL, up to 85.3% using Ru/C in 1,4-dioxane and 93% using Ru/C in 1-butanol. The combination of both sources of hydrogen was indispensable to achieve significant yields of 2-MTHF. For all the catalysts, the highest 2-MTHF yields were obtained when the best hydrogen donor, 2-propanol, was used as a solvent. Overall, the use of Ni-Cu/Al_2O_3 resulted in 2-MTHF yields of approximately 40% after 5 h and 80% after 20 h.

Impact

The 2030 Agenda for Sustainable Development, adopted by all United Nations Member States in 2015, provides a clear guideline towards the economic, social and environmental sustainability. The aforementioned agenda established the 17 Sustainable Development Goals (SDGs), which are an urgent call for action by all countries - developed and developing - in a global partnership. Among them are those related to the economic growth as well as those focused on subjects tackling a climate change and working to preserve our oceans and forests. Some of those goals can be accomplished by the integration of Green Chemistry Principles and Biorefinery Concept [143]. This work clearly demonstrates that both can be easily integrated and their integration may have a clear positive impact on numerous areas of life. Among them are e.g. environment, human health, economics and business.

In terms of impact of the proposed solutions on environment, are aspects related to the fact that many chemicals end up in the environment by intentional release during use (e.g., pesticides), by unintended releases (including emissions during manufacturing), or by disposal. Green chemicals either degrade to innocuous products or are recovered for further use. Additionally, plants and animals suffer less harm from toxic chemicals in the environment. Also, lower potential for global warming, ozone depletion, and smog formation can be achieved by the use of green chemistry and biorefinery concept. Furthermore, use of biomass as source of novel chemicals allows less chemical disruption of ecosystems as well as contributes to lesser use of landfills, especially hazardous waste landfills.
Hence, this has a direct impact on human health, namely on cleaner air because lesser release of hazardous chemicals to air leading to less damage to lungs can be achieved. Also, cleaner water can be expected because lesser release of hazardous chemical wastes to water leads to cleaner drinking and recreational water. Furthermore, by the implementation of green chemistry principles, an increased safety for workers in the chemical industry can be expected since less toxic materials are in use, less personal protective equipment are required and less potential for accidents (e.g., fires or explosions) can be foreseen. Consequently, safer consumer products of all types can be obtained. In this sense, new, safer products will become available for purchase and some of those commodities will be made with less waste or some products (i.e., pesticides, cleaning products) will be replacements for less safe products.
Finally, the above-mentioned aspect has a direct impact on economy and business because higher yields for chemical reactions can be attained due to consuming smaller amounts of feedstock to obtain the same amount of product. Due to less synthetic steps, often allowing faster manufacturing of products, increasing plant capacity, and saving energy and water, economy of the process is definitively more favorable. At the same time, waste reduction, elimination costly remediation, hazardous waste disposal, and end-of-the-pipe treatments is additional economic benefit for the process. The use of waste as new feedstock allow replacement of a purchased feedstock contributing to favorable economics of these new businesses. In addition, due to better performance, less substrates are needed to achieve the same function. Furthermore, reduced manufacturing plant size or footprint through increased throughput is additional impact on economics of the process.
Therefore, the use of biomass processed according to the green chemistry principles demonstrates a great potential for different areas with a positive impact on society.

Conclusions

The development and usage of greener solvents are topics emerging in the recent years, due to the increasing concerns about pollution and climate changes. In this context, more sustainable solvents coming from natural sources can also reduce the dependence of petrochemicals that are harmful, toxic, and environmentally damaging. The literature is full of examples of methods for the biomass conversion into chemicals and, in many cases, the authors claimed for a synthesis of they as potential green solvents and building blocks. However, there are controversies in the use of hazardous and petrochemical derived solvents and catalysts during these compounds obtaining. Among the various technologies described, the ideal in the green chemistry concept would be the use of residual biomass combined with heterogeneous recyclable catalysts and renewable solvents. The successful use of economically and environmentally sustainable solvents depends not only on the source of them but also on their properties to facilitate product/catalyst isolation and reaction workups, improving in reaction yields and reduction of environmental issues.

Conflict of interest

There are no conflicts to declare.

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SPELT VS COMMON WHEAT: POTENTIAL ADVANTAGES AND BENEFITS

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Abstract
This work gives a brief review of existing studies that compares spelt and modern wheat from various aspects of quality including technological, nutritional, functional and safety performance. Spelt shows acceptable bread-making performances. It can be used for bread, cookie, cracker and pasta manufacture with some adaptations in processing. Regarding nutritional quality, spelt is very similar to wheat and represents richer source of selenium, folates, phytosterols and alkilresorcinols than modern wheats. From the aspect of food safety, spelt shows advantages as being a hulled wheat.

Keywords
spelt, common wheat, advantages, food safety

Introduction
Spelt *(Triticum aestivum ssp.* spelta*)* is a hulled form of bread wheat *(Triticum aestivum)* and belongs to a hexaploid series of the Triticum genome. Spelt is considered a subspecies of the *Triticum aestivum* because of large genetic similarity between them. The only difference is in the hulled character of the spelt grain which is regulated by mutations at solely two genetic loci [1]. Scanning electron micrograph (SEM) of spelt spikelet cross-section showed that spelt wheat has hard hulls clinging tightly to the grain [Fig. 1].

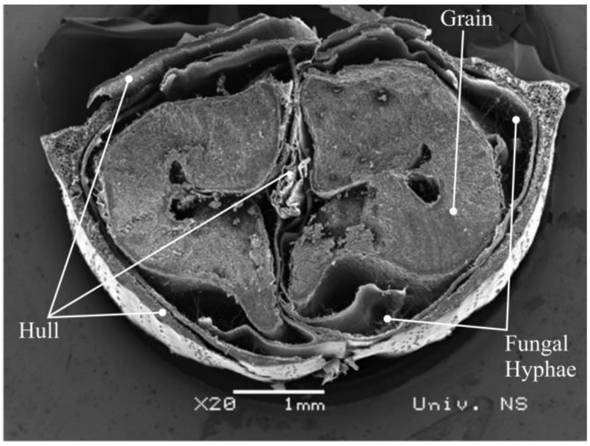

Fig. 1. SEM of spelt spikelet cross-section (× 20 magnification). *Source: [2]*

Spelt belongs to the group of the, so called, ancient wheats [3,4]. Among other ancient wheats, emmer and einkorn, spelt is chronologically the „latest“ as hexaploid wheat species appeared thousand years later than the diploid (einkorn) and tetraploid (emmer) wheats. Spelt is a cross between emmer and bread wheat [5].

Ancient wheats have great potential for cultivation under organic, bio-dynamic or low-input farming conditions. The great interest of consumers for ecologically grown food that supports sustainable crop production has led

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to the rediscovery of ancient wheats cultivation. Spelt production has been increased in recent years [6]. Spelt has been readily chosen by organic farmers and has became an alternative crop to common wheat, especially where conventional wheat varieties adapted for organic production are lacking [7]. The suitability of spelt to low-input farming is due to its better adaptation to a wider range of environments [4].

Another reason for the renewed interest for ancient grains is that, unlike modern wheat, they were not subjected to extensive genetic improvements directed towards enhancement of numerous agronomic and technological quality traits such as yield increase, high loaf volume capacity for bread production, high gluten content for pasta production, reduced susceptibilty to diseases and insect attack, increased tolerance to environmental stresses, homogenous maturation, etc. [4,8]. Numerous concerns exist in relation to the undesirable effects of intensive breeding programmes on nutrient composition and allergic potential of modern wheat. There are indications that substantial decline in nutritional and nutraceutical attributes as well as an increase in gluten immunoreactivity of modern wheats may be associated with breeding intervetions. Moreover, clinical studies exert that modern wheats produce higher inflammatory response in patients and healthy subjects and have impaired antioxidant potential in comparison to ancient and heritage wheats [9]. Due to lack of human intervention, the genetic diversity of ancient wheats population is much larger than that of modern wheat. Ancient wheats populations are made of heterogeneous, closely related strains referred to as land races whereas modern wheat consists of homogeneous strains as a result of breeding [8]. Greater diversity of populations of old wheats is related to their better adaptability to harsher growing conditions and poor soils [4] and may be useful in withstanding the stresses caused by ongoing climate changes.

There have been claims that ancient wheats have better nutritional and nutraceutical properties than modern wheats [4]. In addition, ancient wheat grains were anecdotally reported to be better tolerated by consumers suffering from various forms of sensitivities or intolerances to wheat proteins. Many of these claims lack scientific substantiation but some scientific studies supported the existence of differences between modern and old wheats regarding nutritional composition and allergenic potential. On the other hand, there also exist contrasting studies that do not support these conclusions. Controversial results gained increasing attention of researchers that resulted in several detailed studies and critical reviews on the available information regarding the differences between modern and traditional wheats in their composition and health benefits [3,4,8]. Studies that focus on searching for biological markers that may help discerning between organically and conventionally grown wheat may also complement the knowledge regarding the differences between ancient and modern wheats. Moreover, to get a more complete insight into the potential advantages of old wheat grains, it is necessary to consider the role of hull in protecting the grain from harmful environmental influences such as the accumulation of pollutants and mycotoxins.

Economic viability of spelt could be improved by using new innovative technologies aimed at improving the use of waste materials from spelt (straw, chaff) or recovering valuable compounds from them [10, 11]. Cereal husk can be used to replace wood in manufacturing composite materials for automobile, packaging and construction industries [12]. Spelt husk was found to be a suitable alternative filler to replace soft wood in reinforcing composite materials, providing 15% better strength than wood components [12]. Spelt contains more gluten than modern wheat, but its performance in bakery and pasta industry is poor. However, it might have potential for use as an edible coating to prevent oil uptake during deep-frying [13]. As particularly suitable for cultivation in organic farming systems, spelt kernels are suitable for production of sprouts. Pulsed electric field treatment was found efficient in stimulating the growth, increasing the strength and optimizing the nutrient composition (higher content of total phenolics, minerals, free amino acids, carotenoids, chlophylls, soluble proteins) of wheat sprouts [14].

This work attempts to give a brief overview of technological and nutritional characteristics as well safety concerns of spelt wheat compared to modern wheat.

Technological quality of spelt wheat

Although spelt is a bread wheat, its breadmaking potential is inferior in comparison to modern wheat. Many studies showed that spelt doughs are difficult to handle due to noticeable softness, increased adhesivity, low stability to mixing and low oven rise which result in poorly developed bread crumb and low loaf volume [15, 16, 17]. On the other hand, there are positive reports that demonstrated the suitability of spelt in breadmaking [18, 19] and comparable bread quality to that of modern wheat. Lacko-Bartošová and Rédlová [20] noted that

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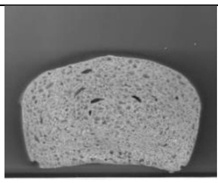
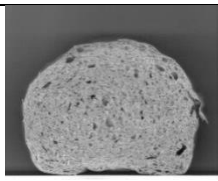
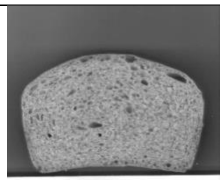
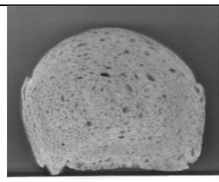
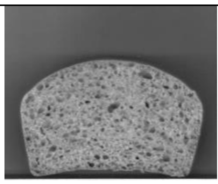
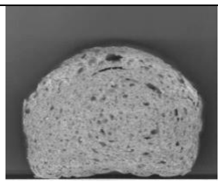
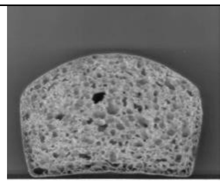
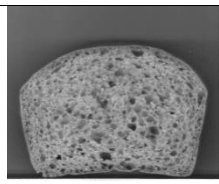
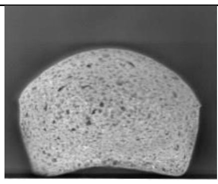
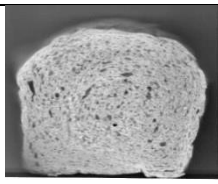
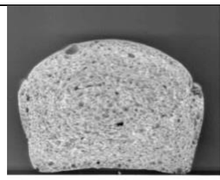
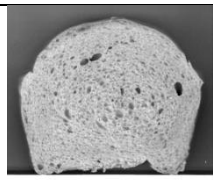
genetically pure spelt varieties have diminished baking potential whereas spelt varieties resulted from inter-breeding with bread wheat have acceptable baking performance. The baking performance of spelt is mainly driven by the quality of gluten proteins [21], but not on the their quantity [22]. In a later work, Schober et al. [21], proposed a classification of spelt wheat into 3 groups: group 1 would be spelt varieties crossed with modern wheat; group 2 would be typical spelt varieties and group 3 would be weak spelts unsuitable for food applications. The bread-making performance of spelt wheat can be improved by the use of additives suitable for organic products (ascorbic and citric acid, xylanase) (Table 1) [22].

Table 1. Effect of improvers on crumb structure of spelt breads. *Source: [22]*

Spelt genotype	**Improver treatment**			
	Control	**TG**	**GOx**	**ASC**
Genotype 1				
Genotype 2				
Genotype 3				

TG, transglutaminase (dose 1.5 U/g flour); GOx, glucose oxidase (0.1 g/kg flour); ASC, acorbic acid (0.2 g/kg flour).

In the study on the breadmaking properties of dominant spelt varieties in Serbia, it was demonstrated that, among all tested improvers (ascorbic acid, glucose oxidase and transglutaminase) they showed the highest response towards ascorbic acid. The same study confirmed that the spelt varieties with better genetic potential for breadmaking had higher response to the action of improvers. To sum up, some adaptations in the bread-making process are necessary when using spelt: higher doses of ascorbic acid, shorter mixing time and longer resting times with frequent roundings [23].

Spelt wheat is suitable for other uses, particularly cracker and cookie manufacture because these applications require weaker gluten properties. Spelt showed better cracker-making performance compared to common wheat as it yielded less deformed, soft and thin crackers [24]. Within spelt varieties of different baking potential, better performance was exerted by „stronger“ spelt varieties in comparison to the „weak“ ones as they exhibited higher oven rise and conversely yielded well-developed crumb and flaky cracker structure [24].

<u>Nutritional properties and health benefits of spelt wheat</u>

Spelt has gained an image of „healthier, more natural, less over-bred“ cereal in comparison to modern wheat [21]. Myriad of studies reported that spelt is higher in proteins, lipids (especially Δ^7-avenasterol) and minerals (Mg, P, Fe, Cu, Zn) than conventional wheat [25]. Bonafaccia et al. [26] reported that spelt wheat was higher in soluble fibres and proteins in comparison to standard bread wheat and durum wheat. But, the same authors found that spelt bread contained more rapidly digestible starch that wheat bread. On the other hand, Abdel-Aal and Rabalski [27] reported that wholegrain flours from commercial spelt varieties contained 8-10 times higher

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amounts of resistant starch in comparison to modern wheat. The drawback of the majority of these reports was that they did not account for environmental differences and compared grain samples obtained from different locations and origins, commercial samples, samples with no indication of origin etc. Grain composition is strongly influenced by genotype, environment, their interaction and farming method (organic or inorganic). Therefore, only studies that minimize the impact of environment and compare varieties grown together under same treatments can provide relevant information [4,6]. In this respect, the largest body of data on the composition of ancient and modern wheats grown under the same environmental influences, collected within the frame of the EU HEALTHGRAIN project (2005-2010), allows the comparison of 5 lines of einkorn, emmer and spelt together with 161 modern wheat varieties regarding the content of dietary fibres and phytochemicals (minerals, trace elements, polyphenols, carotenoids, folates, sterols, alkylresorcinols, betaine, choline) [3]. From this dataset, it can be concluded that spelt wheat contained less total fibres, less total phenolic acids, slightly less total tocols, α-tocopherol and ferulic acid but higher content of folates, alkylresorcinols and phytosterols in comparison to modern wheat [4]. It was also shown spelt contained higher concentrations of selenium [28]. Spelt was reported to be the lowest in phytic acid by 40%, compared to modern wheat [29], which is particularly important for the bioavailability of minerals. Bodroža Solarov et al. [30] reported that there were differences in the non-saponifiable lipid fractions in the set of 7 bread wheats and 10 spelts and suggested the adequacy of this parameter as a tool in discerning between common and spelt wheat. Similarly, Righetti et al. [31] found best discrimination between spelt, emmer and einkorn using alkylresorcinols. Brandolini et al. [32] found that bread wheats *(T. aestivum* and *T. aestivum* spp. spelta) contained high amounts of bound phenolic acids in comparison to *T. monococcum* and *T. turgidum*. Ferulic acid was dominant in all tested samples. Phenolic acids were not uniformly distributed in the kernel: they were abundant in bran and germ but rare in the endosperm.
In spite of the general perception of spelt as a healthy cereal, there is little scientific evidence for the definite support of this statement. Dinu et al. [4] presented a review on the health effects of ancient wheat species taking into consideration existing data from in vitro studies, animal models, immune toxicity studies and human studies. In an animal model using diabetic fatty rats [33], the effects of diets based on emmer, einkorn and spelt on the onset of type 2 diabetes mellitus were investigated. Development and progression of diabetes was less pronounced in the group fed by ancient wheat grains as compared to those fed by refined *T. aestivum*. Spelt was reported to significantly improve glycemic index. This contrasts the earlier finding of Marques et al. [34] who observed similar glycaemic profile for spelt and refined wheat bread in healthy subjects. Spelt bread was reported to have high glycaemic index of 93±9 [34]. In a human study conducted on wheat allergy sufferers (Baker's asthma), it was suggested that spelt is potentially hypoallergenic wheat that could be tried in patients with wheat allergies as it produced less allergenic response [35].On the other hand, cytotoxicity of spelt was confirmed in the studies of Vincentini et al. [36, 37] and van der Broeck et al. [38] and was similar to that of *T. aestivum,* therefore it cannot be recommended to coeliac sufferers.

Epidemiological and intervention studies showed that consumption of wholegrain cereals is associated with a range of positive health effects and indigestible dietary fibres were emphasized as major contributors to this effect. Some authors suggest that not only fibres but numerous other bioactive compounds (proteins, microelements, ferulic acid) present in the aleurone layer of bran have their role in health-promoting activities [39]. Spelt was reported to produce similar yields of fine and coarse bran fractions during milling but aleurone layer contained in the spelt bran had higher amounts of lipids and unsaturated fatty acids as well as minerals [40]. The spelt aleurone layer was indicated as a possible marker to discriminate between modern and spelt wheat.

Protective effect of hull in spelt wheat

The presence of hard adherent hull is believed to protect the grain from harmful environmental effects such as accumulation of pollutants and mycotoxins as well as insect damage. Spelt wheat is less prone to fungal infestation owing to higher stalk and hulled kernel [41].
But cultivation under organic conditions without the use of conventional crop protection agents may increase the risk for the occurrence of fungal infestation and consequent mycotoxin accumulation in spelt grains. Data on spelt fungal contamination is not abundant, but lately it has been in the focus of researchers. Moudrý et al. [42] investigated and compared 23 varieties of hulled wheat (emmer, einkorn and spelt) with landraces and modern wheat in organic cultivation and observed that the hull-less whets were less prone to fungal diseases (mildew and brown rust) and accumulated less DON. Krulj et al. [43] reported lower incidence of grain infestation with *Fusarium* spp. and *Alternaria* spp. in spelt than in modern wheat. The majority of studies imply that hull exert a protective role against accumulation of fungal toxins but only to a certain extent. Mankevičiene et al. [44]

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investigated the occurrence of several mycotoxins (DON, ZEA, T-2/HT-2) on organically cultivated spelt and common wheat. It was concluded that hull provided certain protection as the concentration of examined mycotoxin was the lowest in dehulled spelt whereas hulls were highly contaminated with the toxins. Similar conclusion was made by Suchý et al. [45] who examined the accumulation of toxins produced by *Fusarium* spp. and *Alternaria* spp. but it was outlined that the protective effect of hulls is only partial. Protective effect of hulls against fungal contamination and accumulation of Alternaria toxin was inferred in the study of Vučković et al. [46]. Zrcková et al. [47] concluded that hulls represent an important factor of passive resistance against *Fusarium* spp. infection. It seems that tight and hard hulls represent a mechanical barrier to the propagation of fungal hyphae in the spikelet tissue. The authors propose secondary protective mechanism: narrow opening of the flowers of hulled wheat may reduce the entry of fungal spores to flowers. Suchowilska et al. [48] investigated the mycotoxicological profile of einkorn, emmer and spelt after artificial inoculation in the field with *Fusarium culmorum* and concluded that the ability of grains to accumulate toxins is species specific i.e. the wheat species differed in their resistance towards *Fusarium* infestation. Spelt hulls efficiently protect grains from *A. flavus* infestation and their toxicological metabolites [49]. Krulj et al. [2] investigated the effect of storage conditions on accumulation of aflatoxin B1 in spelt grains and observed that water activity was more important factor than storage temperature for toxin accumulation. In addition, husk removal prior storage decreased the toxin accumulation and distribution. Low-temperature plasma is an emerging new technology that was reported to successfully reduce the number of fungal colonies on stored wheat grains and positively affect germination process and initial growth of germinated seeds [50]. Selective heating with radio frequency energy was effective in destroying storage insects (rusty grain beetle) in wheat grains without causing harmful effects commonly induced after thermal treatment [51].

Table 2. Distribution of AFB1 in hulls and dehulled grains of wheat samples. *Source: [2]*

Code	**Variety**	**Samples**	**AFB1 concentration (µg kg^{-1})**		
			Control	***Aspergillus flavus* No. 1**	***Aspergillus flavus* No. 2**
SH	Spelt	Hulls	7.10±0.20^{a}	648.03±23.07^{d}	97.34±3.09^{c}
SDG		Dehulled grains	<LOQ*	256.46±12.81^{c}	30.68±5.34^{b}
CWH	Common wheat	Hulls	<LOQ	18.30±0.29^{a}	4.83±0.33^{a}
CWDG		Dehulled grains	<LOQ	<LOQ	<LOQ
HWH	Hybrid wheat	Hulls	<LOQ	49.10±1.59^{b}	109.54±1.82^{d}
HWDG		Dehulled grains	<LOQ	<LOQ	<LOQ

Impact

Increasing pressure for transition in agricultural practise caused by upcoming climatic changes and growing human population has led to the renewed interest for low-input wheat varieties. Spelt is a hulled subspecies of wheat bread that has been cultivated as a marginal crop on small areas in Europe and north America. It became an interesting alternative to modern wheat due to its good adaptability to different environments and suitability for organic cultivation. It has been evidenced from previous studies [52] that various forms of farming systems (organic, biodynamic) other than conventional have positive ecological impact due to noticeably reduced ecological footprint per product unit. Attempts to introduce and popularise organic crops greatly contribute to increased biodiversity and formation of ecosystems more durable and able to sustain changing environmental conditions. Besides positive environmental impact and high biodiversity, growing organic crops contribute to production of wholesome, naturally nutritious food without the need for industrial fortification and excessive rafination. Part of the results sublimated in this opinion paper has been produced as a result of national project III 46005, funded by the Serbian Ministry of Education of Science and Technological Development over period from 2011 to 2019. In Serbia, spelt cultivation area in this period has increased by 10 times. Also during this period, dozens of new innovative spelt-based products appeared on the Serbian market as the result of research activities carried out within the project.

Conclusions

Data available until today on the composition and health benefits of spelt and other ancient wheats does not allow definite conclusion that these varieties are superior in comparison to the conventional wheat mainly due to lack of adequately designed comparative and clinical studies. Nevertheless, available information is positive and demonstrate that spelt is a richer source of some bioactive compounds (selenium, folates, phytosterols and alkylresorcinols). From agronomic and food safety point of view, advantages of spelt over modern wheats are related to the ability of spelt to grow in unfavourable weather conditions without high-input and the protective effect of hull against accumulation of fungal toxins. Disadvantages of spelt are low yields, more complicated processing due to dehulling step and somewheat lower bread-making performance in comparison to that of modern wheats.

Conflict of Interest
There are no conflicts to declare.

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MODEL AND TECHNOLOGY FOR PRIORITIZING THE IMPLEMENTATION OF END-TO-END BUSINESS PROCESS COMPONENTS OF THE GREEN ECONOMY

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Abstract
The problem of sustainable development of production is directly related to the three components of the "green economy" - economic, social, and environmental. Their harmonious combination makes it possible to obtain results that improve the social relations of both producers and consumers of goods and services. The implementation of the components of the "green economy" is carried out by various projects. The projects are carried out by irregular end-to-end business processes that compete for common resources in the process of their implementation. The impact on the components of the "green economy" is realized by the proposed model and technology. For this purpose, the software tool <ADVISOR DECISION-MAKER> was developed. The use of this tool by the decision-maker employee allows them to find the best solutions for process management. The solution is represented as priorities to access to shared resources by each process. This ensures their fulfillment within the deadlines established by the contracts. The level of innovations, economic indicators, production stability and competitive ability of products in a dynamically changing market is thereby improved. The results of such commercialization of scientific research have an impact on all components of the "green economy".

Keywords
innovations, “green economy”, economic indicators, social sphere end-to-end business process.

Introduction

In contrast to the concept of sustainable development of production, in a "green economy" the development and stability of production is considered from the point if view of simultaneously achieving the social, economic, and environmental goals of a specific corporation or enterprise. This means that when creating a production development strategy focused on achieving certain economic indicators (profit, viability, etc.), the environmental and social components must be considered in complex [1]. The implementation of these components is carried out in the form of relevant projects. For each of such projects, a set of measures is drawn up. This is required to develop a model that would ensure the transition of production to a "green economy" and reorientation of its economic, environmental, and social components. The complex of such measures can be represented as a set of economic, environmental, social, innovative, irregular, end-to-end business processes (BP) competing for common resources during their implementation. The problem of managing such BP of corporations and enterprises is related to the fact that such processes do not use existing hierarchical approaches for the distribution of resources between their units [2]. This circumstance leads to competition for resources between BP, failure to meet deadlines, and consequently to a subsequent decrease in economic indicators, followed by risks and failure to achieve planned results in the economic and social spheres [3,4].

BP are represented by the appropriate sequence of actions. To manage BP, their detailed description is required for different environmental conditions, considering the access of each process to resources (competition for resources between processes that run at the same time). Such a requirement makes it difficult to develop their

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models as it is necessary to consider the set of possible cross-functional sequences of actions that allow achieving the goals of these processes and the resources necessary to complete these actions. When determining the workflow, the necessary and sufficient conditions for such a description are identified. A necessary condition is its presentation in the form of admissible sequences of actions that ensure the achievement of a local goal regulated by the rules of operation of the enterprise, etc.

The conditions that are sufficient are those under which the process is running only if the appropriate resources are available at the time the action starts. The determination of the sequences of actions (workflow) is carried out both by means of the information-analytical system (IAS) and by the actions performed by the DM [5,6]. At the same time, the data necessary to support tasks is transmitted by the information system between the performers for the implementation of management functions.

Formally, such a description of the BP enables to define the overall workflow as a conjunction of possible trajectories for its implementation. The rationale for choosing such a description of BP is that it allows representing both separate process and many parallel end-to-end processes as a set of trajectories. With this, it becomes possible to predict the use of resources only for a subset of the permissible current trajectories of each business process without considering all the trajectories, which increases the efficiency of forecasting the results. The advantage of this approach is improved coordination of the activities of various commercial entities within a single end-to-end process. This leads to the removal of barriers between divisions, helps to reduce the time and material costs that in turn improves the value of economic indicators of management objects. In addition, the employees are oriented towards the result. Consequently, the improvement of the social and psychological climate at the facility is ensured.

Methods

The unsolved problem of process management by end-to-end BP is the complexity of the systemic presentation and understanding the incorrectness of their taking place [7]. Therefore, when forming possible sequences of actions for implementing end-to-end BP, the sequence that can only be performed with available resources should be selected. In fact, this sequence of actions displays workflow descriptions of the end-to-end business process [8,9,10]. In this regard, it is necessary to develop such a model of end-to-end BP that would make it possible to represent the state of the process at a formal level in the form of qualitative or quantitative parameters [11,12]. If the output parameters of BP do not correspond to commercial conditions, then it is necessary to find a solution that implements their transfer into the required state [13]. Such a decision is presented in the form of establishing priorities for access to the shared resources of competing BP that would ensure their implementation within the time frames established by the contracts [14,15].

At the same time, the composition of BP can change at some competitive points. This means that at some competitive point a business process may be included in the group of executed BP that do not compete with them for resources at previous points [16,17,18]. This problem is similar to the problem of the third machines. However, when the number of competitive points is equal to 4 or more, it is extremely difficult to solve this problem with classical methods [19,20,21]. Therefore, we propose a model and technology to prioritize and initiate end-to-end BP at all competitive points, taking into account their normative and remaining time for performing actions of fixed IAS in the event log, both in automatic mode using the developed software <ADVISOR DECISION-MAKER> and with the involvement of the decision-maker. This tool provides support for the process of obtaining various variants of solutions for management of the end-to-end BP in the form of setting priorities for their initiation using the developed set of nested macros. The resulting solutions are provided by the decision-maker (DM) to find the best option for each order, in accordance with their current restrictions. The macros provide appropriate calculations and initiation of the platform, followed by saving the result in the database and the corresponding tables.

As shown by the practice of no more than 3 options, when finding the required solution, the DM can choose, from the group of end-to-end BP those which are the most important/key for an object, which must be fulfilled, as they directly affect its economic, environmental and social indicators. The need to obtain such a solution arises from situations related to the inclusion of a new project/order, failure or replacement of equipment, lack of materials, human factors and other types of incidents. In this connection, it is required to find appropriate priorities for their implementation. The DM can also choose and add to the platform those competitive points that are needed for subsequent calculations.

The aim of the study is to develop a model and technology for finding solutions for the implementation of economic projects implemented by non-regular, end-to-end BP competing for common resources, while fulfilling the restrictions imposed on them.

Results and discussion

The task of management for the end-to-end BP is to find the sequence of their execution at competitive points in order to minimize the waiting time of resources with restrictions on the execution time of each of these processes, as well as the waiting time for their access to resources. Process management means obtaining the required solution in the form of an ordered set of sequences of all actions of BP in all competitive points.

To develop a model for finding such a <Solution>, we introduced the following notations:
$Z(s)=(z_1,z_2,...,z_{c^z(s)})$ is the group of projects/orders at the *s*-th competitive point, where z_i is the *i*-th order of the group $Z(s)$ of orders at the *s*-th competitive point, $C^z(s)$ is the number of orders in the group $Z(s)$. Fulfillment of the commercial order within the limits of its life cycle is carried out by the relevant BP:

$$Z_i=(B_1^i,B_2^i,...,B_l^i,...,B_{c_i^B}^i) \ ,$$

where B_l^i is *l -th* business process of the *i-th* order, C_i^B - the number of BP implementing the *i-th* order.
In doing so, each *l-th* business process is performed by a sequence of appropriate actions

$$B_l^i=(D_{l1}^i,...,D_{lj}^i,...,D_{C_l^D}^i),$$

where D_{lj}^i is the *j-th* action of the *l-th* business process of the *i-th* order, C_l^D the number of actions in the *l-th* business process of the *i-th* order in the group $Z(s)$. At the same time, the implementation of BP B_l^i is associated with the following temporal parameters:
T_i^{set} – is the execution time of the *i*-th order under the contract,
t_i^{lefi} – is the remaining execution time of the *i*-th order
$t_{lj}^{i(h)}$ – is the normative (standard) execution time of the *j-th* action of the *l-th* business process for the relevant *i*-th order,
$t_{lj}^i(C_l^D)$ – is the execution time of the *j-th* action of the *l-th* business process for the *i*-th order.

The waiting time for each subsequent action is determined by the execution time of the previous action since the subsequent action can only be performed when the resource used by the previous action is released.
The resource restrictions associated with the waiting time of the corresponding business process are represented by the following expression:

$$min(t_{lj}^{i(wt)})/\forall B_l^i \quad t_l^i \le t_i^{i\,max} \ , \tag{1}$$

where $t_{lj}^{i(wt)}$ – is the waiting time for resources to complete the *j-th* action of the *l-th* business process for the *i-th* order B_l^i;
t_l^i – is the time of execution for the *l*-th business process of the *i*-th order;
$t_l^i \le t_i^{i\,max}$ – is time limit for execution of the *l-th* business process.
Then the D_{lj}^i model for describing the actions of the *j-th* action for the *l-th* business process of the *i*-th order is represented as follows:

$$D_{lj}^i=(t_{lj}^h,t_{lj}^i(C_l^D),t_l^{i(wt)},t_i^{lefi}) \tag{2}$$

The corresponding business process of the *i-th* order will be considered completed if the execution time of the *j-th* action is greater than or equal to zero

$$t_{lj}^{i}(C_l^D) \geq 0, \forall i \in C^Z(s), j \in C_l^D, l \in C_i^B . \tag{3}$$

The actual and remaining execution time will also be greater or equal to zero.

$$(T_i^{max} - T_i^{set}) \geq 0, \forall i \in C^Z(s), t_i^{left} \geq 0, \forall i \in C^Z(s). \tag{4}$$

Depending on the temporal parameters of the *l-th* business process at each *s-th* competitive point, it is necessary to find the optimal priority of their passage P_{ls}^i.

In accordance with the task, the model for finding the priorities of the passage of the *l-th* business process at the *s-th* competitive point can be represented as a tuple:

$$M = (T_i^{set}, t_i^{lefi}, t_{lj}^i(C_l^D), t_{ij}^h, P_{ls}^i). \tag{5}$$

The process of finding the optimal <Solution> is implemented by the technology being developed using this model while performing the following objective function:

$$\tau_{Z(s)} = \sum_{i=1}^{C^Z(s)} \sum_{l=1}^{C^B} (T_l^{iset} - T_l^{i\,max}) \to \min_{T_l^{iset}, T_l^{i\,max}} \tag{6}$$

To find the <Solutions> options (control actions) in the form of prioritizing access to the common resources of competing BP at the corresponding competitive points, which would ensure their implementation within the deadlines established by the contracts, the technology for their production is proposed. For example, when carrying out a group of economic projects, such common resources at competitive points may be human resources (a specialized team equipment installers performing installation work in several projects simultaneously). Doing so, we will take into account that the composition of the BPs can change at some competitive points. This means that a business process that does not compete with them for resources at previous points can be included in the group of executable BP. The process of finding the required <Solution> proposed is to be carried out in automatic mode using the software tool <ADVISOR DECISION-MAKER> and in a combined way with the inclusion of a decision-maker (DM) in such a process. To perform this, we use the following criteria: the remaining execution time of BP/orders and the time delay for their completion. The determination of the required <Solution> is carried out by several runs in automatic mode, and upon receipt of a negative result, the <Solution> DM is adjusted with the subsequent fixation of the 1st, 2nd, 3rd, and 4th competitive points. The proposed technology is implemented in the following steps:

Stage 1. Generation of the initial data (the start and end time of the order execution, normative (standard) time $t_{lj}^{i(h)}$ for the action of the business process and waiting time $t_{lj}^{i(wt)}$ it takes for it to access the resources). The time parameters for each BPs are taken from the projects, and data on the resources for which they will compete (human resources, equipment, materials, etc.) and at which competitive points from the relevant regulatory documents.

Stage 2. Calculation of the duration of the *j-th* action for the *l-th* business process of the *i-th* order at competitive points in the form of the sum of two components:

$$t_{lj}^i = t_{ij}^{i(h)} + t_{lj}^{i(wt)}$$

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The determination of the remaining execution time for each *i-th* order is carried out by subtracting from the execution time under the contract the execution time of the *j-th* action of the *l-th* business process of the *i*-th order:

$$t_i^{left} = T_i^{set} - t_{lj}^i .$$

Stage 3. Calculation of the values of the total remaining execution time of all orders according to the appropriate sequence of priorities:

$$T = \sum_{i=1}^{N} t_i^{left}$$

Stage 4. There should be set in automatic mode the priority of starting orders at the 1-st competitive point in the 1-st run, meeting the criterion of the maximum total remaining execution time $T_l^{S\,max}$ of the corresponding BPs. By analogy, the values of its deviation from the largest $T_l^{S\,max}$ and current T_l^{Scur} in all priorities d_i are successively calculated at each subsequent competitive point. They determine to what extent the remaining time will change when initiation (launch) priorities change at subsequent competitive points:

$$d_l = T_l^{S\,max} - T_l^{Scur}$$

Step 5. Correction by the DM of priorities sequences after the first run. Based on the miscalculation results at each competitive point obtained, the DM determines whether the conditions for the absence of negative values of the remaining business process execution time $T_l^{Scur} > 0$ are met. If the conditions are met, then the obtained sequence of priorities is defined for initiating the BP at the corresponding competitive points. If these conditions are not met or the obtained sequence of priorities for some reason does not satisfy him, then the DM will continue to correct it.

Step 6. The determination of the initiation (start) priorities in the 2nd run is carried out using the criterion of the maximum delay in the execution of the BP. Its values are determined by the sum of the remaining time values t_i^{lefi} of the corresponding order in accordance with all options for establishing priorities at the last competitive point, based on the results obtained after the first run. In the presence of negative values, recalculation I automatically carried out. As a result, the order is determined for which the value of the delay time is the maximum. In this regard, this order must be initiated (launched) earlier. To accomplish this, the procedure "raising the priority of the order" is proposed. The procedure's essence is to determine such an order, the priority of which must be increased by one at the corresponding competitive points (to raise the order one level up), thereby assigning a new initiation (launch) priority. At the competitive points where this business process has the first priority of initiation (launch), their existing priority does not change. After the calculations performed by the platform, taking into account the results of the procedure "raising the priority of the order", the corresponding priority for each order is automatically and sequentially established at each competitive point. If after the calculations have been made there are negative values of the remaining time T_l^{Scur} for their execution, then this indicates a failure to fulfill the conditions of the orders and the absence of the <Solution> required.

Stage 7. Correction of the DM **i**n the 3rd run of priorities sequences with fixing in the 2nd competitive points. Based on the data obtained, the DM determines which order should be moved up by priority according to the criterion of the maximum delay for each order. After that, the platform automatically recalculates the sequence of priorities in the remaining competitive points to determine the priority with the longest remaining execution time.

Step 8. Correction of the DM of priorities sequences after the third run. The DM considers all possible options obtained after changes in two competitive points, by fixing the first with subsequent changes in the other remaining points. All calculations for the remaining total execution time are carried out automatically based on the determination of possible priorities at competitive points and orders, the priority of which must be changed. According to the results of the data, the DM makes <Decisions> on choosing the best sequence

Stage 9. Initiation (Launch) of the fourth run, determines the possibility of finding the best result by fixing the 3rd competitive points, by the criterion of the value of the greater total remaining time than found after the run in the third stage. Each priority that was selected during the third run had certain d_i values. Sequentially established orders with their d_i values determined the total value d_s, $d_s = d_I+d_{II}$ according to the results of the 3rd run. Based on the obtained comparisons between the remaining runtime t_i^{lefi} and the total value of d_s, a search is made for such options of priorities at each stage of the runs, in which the total value of d_s will be less than the best result after the run in the third stage. Then the DM sorts out all the launch options that satisfy the given conditions with the search for such priorities wherein the total value of d_1, d_2, and d_3 will be less than d_s obtained after the 3rd run.

Stage 10. Finding the best option of the sequence of priorities for execution orders as to all competitive points by fixing the next fourth point is impossible due to the fact that the condition is not less than or equal to ds obtained after fixing the 3rd points. When fixing the 4th point, this value will *only* increase, which indicates the receipt of the worst decisions.

Verification of the developed model and technology is carried out on the example of fulfillment of orders for manufacturing products by medium and large printing enterprises. Those are the enterprises with a discrete type of production, realizing both periodic and non-periodic (re-emerging) new orders at the same time. The group under consideration consists of 3 projects / orders competing for common resources. The first order is a book, the second a brochure and the third is a magazine. During this testing, the software developed by <ADVISOR DECISION-MAKER> was used. When developing the <ADVISOR DECISION-MAKER> tool, Visual Basic language was used. During the development process, 265 macros were written. Using this tool, enables to get the optimal sequence of execution of orders at the enterprise. The essential problem is that orders competing for resources at corresponding points have different parameters for their execution. Therefore, all possible priorities for launching orders at each competitive point are determined in order to find the optimal priority for their implementation. During this testing, the software <ADVISOR DECISION-MAKER> was used.

In this regard, we formulated the problem to be solved in the form of finding the optimal sequence of possible priorities for launching orders at each competitive point limiting their execution time according to the contracts. In each competitive point, several kinds of orders can be considered, namely, the orders competing for resources at previous points, orders that have completed their own processes and new key orders that have just been sent to production. The key BP are the ones of the highest priority for the company according to their financial indicators, and customers' constancy. Then the start and finish time of each order is recorded at each competitive point, data on the start and end time of the order is recorded, the standard time for the execution of the business process and the time it takes for it to access resources are entered from the database. The criterion for determining the priority of launching each order at the 1st competitive point is the longest remaining time for all orders of all priorities. To determine this, we will form a table of values of the standard execution time of each action for all priorities according to the technological maps in Table 1.

Table 1. Values of the standard time for the execution of BP for all launch priorities at the first competitive point.
Source: Author's research

Orders	Priorities					
	123	132	231	213	312	321
Order1	4	4	8	8	10	10
Order2	8	10	10	4	4	8
Order3	10	8	4	10	8	4

The calculation of the waiting time of the BP at each competitive point is carried out as follows. Since the 1st BP has a standard runtime shorter than the others, its waiting time is 0.

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The execution time of the action of BP $t_{lj}^{i}(C_l^D)$ is automatically calculated by adding $t_{lj}^{i(wt)}$ and $t_{ij}^{i(h)}$. For example, the 1st BP has a waiting time of 0, therefore its execution time is 4, the 2nd BP has a waiting time of 4 (which is the execution time of the 1st BP), the standard time is 8 and, accordingly, its execution time will be 12. The 3rd BP waiting time is found by adding the standard execution time of the 1st and 2nd BP (4 + 8) and its standard execution time which is 10. As a result, its execution time is 22. In addition, the total execution time was determined according to the relevant priorities for starting the BP. For example, the longest total execution time is at the priority 321 and equals 50, which is the worst-case scenario, while the priority 123 is the best because it has the shortest total execution time. Calculations of the BP execution time for all possible priorities and their total execution time at the 1st competitive point are presented in Table 2.

Table 2. Values of the execution time of BP in the 1st competitive point. *Source: Author's research*

Orders	Priorities					
	123	132	231	213	312	321
Order1	4	4	8	8	10	10
Order2	12	14	18	12	14	18
Order3	22	22	22	22	22	22
Total	38	40	48	42	46	50

The calculation of the remaining execution time t_i^{lefi} for each BP in all priorities is determined by subtracting the regulatory runtime $t_{ij}^{i(h)}$ (Table 2) from the execution time of each order under the contract T_i^{set}. For example, for the first priority, when the order execution time is 120,110,100, the remaining execution time for each BP is 116.98.78. In the same manner, these values are calculated for the remaining priorities. The values of the total remaining execution time of the 3 orders are also calculated in accordance with a certain priority of their passage as shown in Table 3.

Table 3. The remaining BP execution time for all priorities at the 1st competitive point. *Source: Author's research*

Execution number	Priorities					
	123	132	231	213	312	321
№ 1	116	116	102	102	90	90
№ 2	98	86	82	108	106	92
№ 3	78	88	98	78	88	98
Total	292	290	282	288	284	280
d_1	0	2	10	4	8	12

The priority 123 of the BPs launch at the 1st control point with a maximum total remaining time of 292 is the most favorable/acceptable since it has the shortest execution time for all orders. To determine how launch priorities will change at subsequent competitive points, we introduce the d_i parameter, which determines deviations from the highest value of 292 corresponding to the current value for all priorities. Accordingly, for 292, the value of d_1 is 0, and for each subsequent priority they are determined by the difference between the highest and the current value (Table 3).The parameter d_i determines the change in the remaining time when adjusting the initiation (launch) priorities at subsequent competitive points. At the 1st run, according to the criterion of the maximum total remaining execution time of the corresponding BP, the priorities for launching of all BPs are set at the 1st competitive point. Also in the 1st competitive point, the best priority is selected to have the value of d_2 equal to 0. According to the d_2 value the remaining execution time of each order is determined. In the same manner, the d_i values are sequentially computed at each subsequent competitive point with the choice of the next best priority from the d_1 passing values of the corresponding point. Thus, using the values of the maximum remaining total execution time of all orders, the optimal priority of passing BP at each competitive point is determined in Table 4.

Table 4. The remaining BP execution time for all priorities at the 7th competitive point. *Source: Author's research*

Execution number	Priorities					
	123	132	231	213	312	321
№ 1	-10	-10	14	14	42	42
№ 2	2	30	38	-14	-19	5
№ 3	26	-7	-23	26	-7	-23
Total	18	13	29	26	16	24

Table 4 presents the total data on the remaining execution time of 3 BPs after passing the last (i.e., 7th) competitive point, determined by the sum of its values for each BP in the respective priorities.
For example, for the 1st BP, according to the corresponding priorities, the values of the remaining time are equal to -10, -10, -23, -14, -19, -23 (-99 in total). We assume that the successful completion of all 3 orders is the condition for the absence of negative values in a certain priority of BP launch. As can be seen from Table 4, this condition is not fulfilled; therefore, the best result where the priority at the 7th competitive point contains the smallest sum of negative values is taken as acceptable. Such a priority is 123 with a value of -10 for the 1st, 2 for the 2nd order and 26 for the 3rd order. In total, this gives the remaining time equal to 18. Nevertheless, in the case of the 1st order, the value is negative, which means the absence of the required <Solution>.
However, this criterion also failed to obtain the required <Solution>, since in all priorities there are one or more negative values. Therefore, the adjustment of sequences of priorities after the first run is carried out by the DM employee of the planning department. Based on the results of miscalculations at each competitive point, the employee determines whether the condition $t_i^{lefi} \succ 0$ is satisfied. If this condition is not fulfilled or the obtained sequence of priorities for some reason does not satisfy him, then the second run is carried out.

To determine the launch priorities in the second run, the criterion of the maximum delay in the execution of orders in all priorities is used. The delay time is determined by the sum of the remaining time values of the corresponding order in accordance with all options for setting priorities at the 7th competitive point, based on the results obtained after the first run. To exclude the occurrence of negative values, the platform automatically calculates the delay time, because of which the order is determined; the values of the delay criterion thereof are minimal. The found order is initiated (launched) earlier using the “rise” procedure, raising the order 1 level up. As a result of calculations, the corresponding priority for each order is automatically and sequentially defined at each competitive point. If negative values are obtained, then this shows the absence of priorities satisfying the conditions for fulfilling orders after the 2nd run.

Similarly, the search for the desired result in the form of adjusting the sequence of priorities for launch orders after the second run is carried out by the DM. Using the values of the total remaining execution time $T_l^{S\,max}$, the DM can change options of sequences of priorities with subsequent storage of them in the corresponding tables for the obtained results to make a detailed analysis of the obtained data. If the required result is not obtained, the DM continues the search for possible options for determining priorities by fixing the 2nd competitive points on the 3rd run. To do this, in two competitive points, the corresponding priority is fixed with the definition of the order, which must be moved up, based on the criterion of maximum delay. The data on the remaining time for all orders of printing products at each fixed point is presented in the column “Remaining time”, fig 1. If the (-) sign appears, then there are no options at such a fixed point that satisfy the order fulfillment condition.

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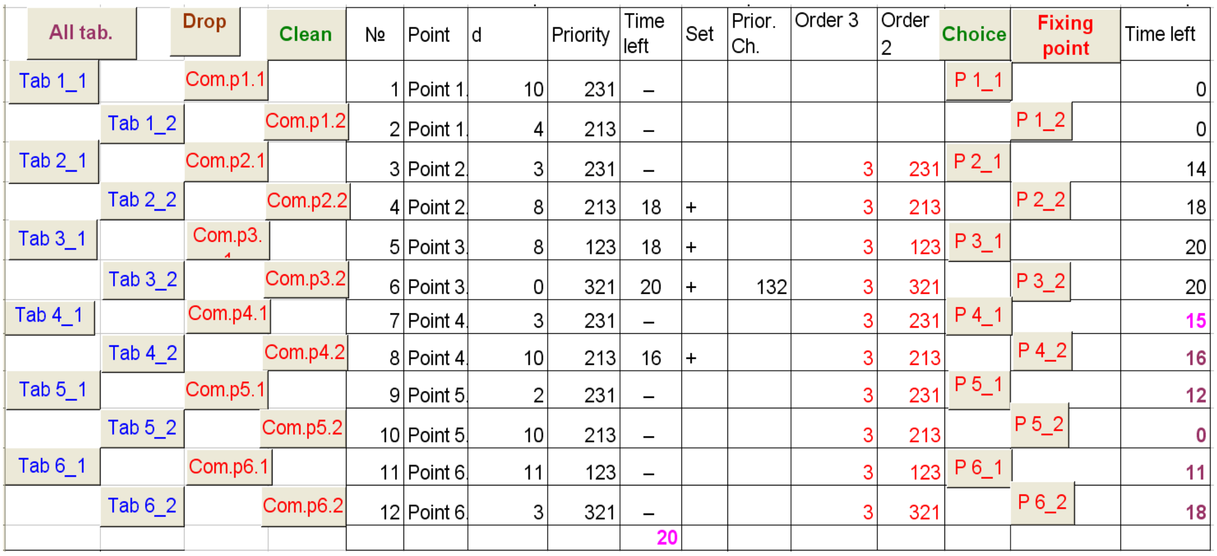

All tab.		Drop	Clean	№	Point	d	Priority	Time left	Set	Prior. Ch.	Order 3	Order 2	Choice	Fixing point	Time left
Tab 1_1		Com.p1.1		1	Point 1	10	231	–					P 1_1		0
	Tab 1_2		Com.p1.2	2	Point 1	4	213	–						P 1_2	0
Tab 2_1		Com.p2.1		3	Point 2	3	231	–			3	231	P 2_1		14
	Tab 2_2		Com.p2.2	4	Point 2	8	213	18	+		3	213		P 2_2	18
Tab 3_1		Com.p3.		5	Point 3	8	123	18	+		3	123	P 3_1		20
	Tab 3_2		Com.p3.2	6	Point 3	0	321	20	+	132	3	321		P 3_2	20
Tab 4_1		Com.p4.1		7	Point 4	3	231	–			3	231	P 4_1		15
	Tab 4_2		Com.p4.2	8	Point 4	10	213	16	+		3	213		P 4_2	16
Tab 5_1		Com.p5.1		9	Point 5	2	231	–			3	231	P 5_1		12
	Tab 5_2		Com.p5.2	10	Point 5	10	213	–			3	213		P 5_2	0
Tab 6_1		Com.p6.1		11	Point 6	11	123	–			3	123	P 6_1		11
	Tab 6_2		Com.p6.2	12	Point 6	3	321	–			3	321		P 6_2	18
								20							

Fig. 1. Data on the total remaining time. *Source: Author's research*

Thus, after the 3rd run is completed, the best option that satisfies the conditions for fulfilling all orders, with the greatest remaining time of 20, is a sequence of priorities for initiating (starting) BP at the corresponding control points. To determine the possibility of a better result, the DM can start the 4th run by fixing the 3rd competitive points according to the total value *ds* obtained from the results of the 3rd run. By comparing between t_i^{lefi} and the total value of *ds*, the search for such variants of priorities at each stage of the run is found, by doing so, the total value of ds should be less than the best result after the run in the third stage. These results are priorities with 20 and d_s equals to 6. Therefore, a search is then made for sequences of initiation (launch) priorities for such a check, in which d_s should be less than 6. Since all options of fixing the 2nd points have been tested, a search is performed of fixing the 3rd competitive points.

The DMs sort out all the launch options that satisfy the given conditions. As practice shows, such options usually find place in the range from 3 to 5, which takes no more than 1-2 minutes. The decision maker, using the d_s value, manually searches for such priorities, in which the total value of d_1, d_2, and d_3 will be less than the value of d_s obtained after the 3rd run. To find the best sequence, first a competitive point is fixed with a minimum d_i value, and then the second and third competitive points with the same values are sequentially fixed. Their values are then summarized and compared with the ds value obtained in step 3. In this case, the condition must be fulfilled under which ds should always be greater. If a variant of determining the sequence of launch priorities that meets the conditions for fulfilling orders is found, then the value of the remaining total time of order fulfillment is compared with the same value obtained in the 3rd run. In this case, after 4 runs with fixing of the 1st, 2nd, 3rd, and 4th competitive points (CP), the sequences are selected in which the remaining time is longer. The resulting data on the remaining execution time for all runs is presented in table 5.

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Table 5. The resulting data on the passage of orders for all runs. *Source: Author's research*

Kod BP	Kod processes	Runs	Name BP	Time general	Time end	Time left
Total: book		Run 1	book	120	130	**-10**
Total: brochure		Run 1	brochure	110	108	**2**
Total: magazine		Run 1	magazine	100	74	**26**
Total: book		Run 2	book	120	123	**-3**
Total: brochure		Run 2	brochure	110	101	**9**
Totall: magazine		Run 2	magazine	100	98	**2**
Total: book		Run 3	book	120	120	**0**
Total: brochure		Run 3	brochure	110	106	**4**
Totall: magazine		Run 3	magazine	100	84	**16**
Total: book		Run 4	book	120	118	**2**
Total: brochure		Run 4	brochure	110	109	**1**
Totall: magazine		Run 4	magazine	100	84	**16**

Analysis of the data in Table 5 allows us to observe the dynamics of improving the options for the resulting solutions. On the 3rd and 4th runs there are no negative values. This means that all orders will be completed on time.

Thus, during the four runs, the <Solution> has been obtained in the form of the best sequence of priorities satisfying the conditions for fulfillment of all orders (Z), presented in Table 6.

Table 6. The resulting sequence of initiation of BP for all 4 runs. *Source: Author's research*

Runs	Competitive points (CP)							Remaining time
	1 CP	2 CP	3 CP	4 CP	5 CP	6 CP	7 CP	
Run 1	123	312	312	231	321	312	213	Z1(-10)
Run 2	123	321	321	213	321	312	123	Z1(-3)
Run 3	123	321	132	321	321	312	213	20
Run 4	123	312	312	231	321	312	213	19

The table shows that the best result was obtained at run 3, according to it, all conditions of the orders were met (there were no negative values), and the total remaining time for all orders was 20 (for the first order 4 hours, for the second 0 hours and for the third 16 hours). During the first and second runs, the conditions were not met, since the delay in the execution time for the first order Z1 was 10 hours and for the second run is equal to 3 hours respectively.

The results of the practical implementation of the task are presented in Table 7. This table displays data on the life cycle of 3 orders (books, brochures, and magazines). For each order, all the necessary data is presented to determine the remaining execution time. The practical implementation of finding the best result is presented and in fact, this data reflects the content of the options for the Decision on the passage of these orders at all competitive points. The storage of these <Solution> in the database of the information system ensures their application in the management of similar orders.

Table 7. Data on the passage of orders at the best option. *Source: Author's research*

Kod BP	Kod processes	Runs	Priority	Name BP	Time process	Time general	Time waiting	Time end	Time left
1	1	Run 3	1	book	4	120	0	4	116
1	2	Run 3	3	book	10	120	13	23	93
1	3	Run 3	1	book	10	120	0	10	83
1	5	Run 3	3	book	14	120	17	31	52
1	6	Run 3	3	book	12	120	10	22	30
1	7	Run 3	2	book	9	120	5	14	16
1	8	Run 3	2	book	12	120	4	16	0
Total: book								120	**0**
2	1	Run 3	2	brochure	8	110	4	12	98
2	2	Run 3	2	brochure	8	110	5	13	85
2	3	Run 3	3	brochure	8	110	16	24	61
2	5	Run 3	2	brochure	10	110	7	17	44
2	6	Run 3	2	brochure	6	110	4	10	34
2	7	Run 3	3	brochure	12	110	14	26	8
2	8	Run 3	1	brochure	4	110	0	4	4
Total: brochure								106	**4**
5	1	Run 3	3	magazine	10	100	12	22	78
5	2	Run 3	1	magazine	5	100	0	5	73
5	3	Run 3	2	magazine	6	100	10	16	57
5	5	Run 3	1	magazine	7	100	0	7	50
5	6	Run 3	1	magazine	4	100	0	4	46
5	7	Run 3	1	magazine	5	100	0	5	41
5	8	Run 3	3	magazine	9	100	16	25	16
Totall: magazine								84	**16**

This is the best sequence of priorities for initiating (starting) BP at the corresponding control points with the remaining value of time equal to 20 as presented in Table 8.

Table 8. The resulting data on the priorities sequences of passing orders at the best option. *Source: Author's research*

Orders	Priorities at competitive points						
	1 CP 123	2 CP 321	3 CP 132	4 CP 321	5 CP 321	6 CP 312	7 CP 213
Order1	1	3	1	3	3	2	2
Order2	2	2	3	2	2	3	1
Order3	3	1	2	1	1	1	3

Figure 2 shows all the possible and optimal sequences for all orders to pass through competitive points after three runs according to Table 2. For the 1st order, the optimal sequence is shown by a bold continuous line, for the 2nd order, the sequence is shown by a bold dotted line, while the 3rd ordering sequence is highlighted by a line consisting of dots.

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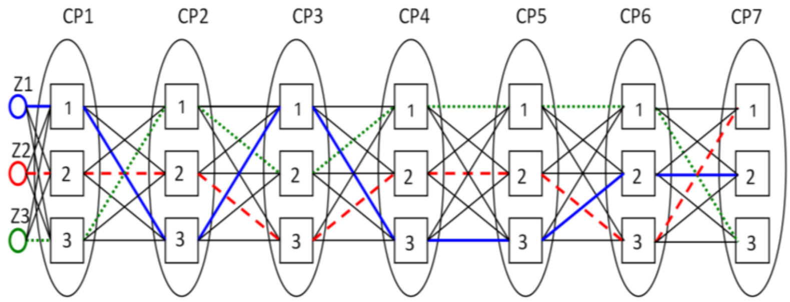

Fig. 2. The resulting traces of sequences of priorities passing by the competitive points of orders.
Source: Author's research

Similar to the example described above, to consider the effectiveness of the developed platform, we will show its work on the example of 10 orders. The portfolio of orders of this group was formed as they arrived over a certain period of time. A prerequisite for all orders is their execution within the deadlines established by the contracts. When forming the order of execution of each order, it is necessary to take into account the time parameters of the remaining orders of the group. In addition, the remaining time for them should be maximum. Table 9 shows the results of calculations using Standard management tools.

Table 9. Execution time data obtained using standard management tools. *Source: Author's research*

Standard management tools	Oders									
	№ 1	№ 2	№ 3	№ 4	№ 5	№ 6	№ 7	№ 8	№ 9	№ 10
Contract time	120	110	100	70	80	75	90	96	95	80
Actual time	134	96	74	60	88	65	85	109	89	71
Time left	-14	14	26	10	-8	10	5	-13	6	9

Based on the results presented in this table, it can be seen that some orders have negative values of the remaining time. The presence of negative time indicates a delay in the completed order, which indicates a failure to fulfill the order on time. This means that the previously assigned requirements were not fulfilled when executing the order portfolio. Failure to fulfill the order portfolio leads to penalties, loss of profits, rupture of contracts, a fall in the image of the enterprise, etc.

Table 10. Data on execution time obtained using Tool <ADVISOR DECISION-MAKER>. *Source: Author's research*

Tool <ADVISOR DECISION -MAKER>	Orders									
	№ 1	№ 2	№ 3	№ 4	№ 5	№ 6	№ 7	№ 8	№ 9	№ 10
Contract time	120	110	100	70	80	75	90	96	95	80
Actual time	120	106	84	60	72	70	75	94	90	76
Time left	0	4	16	10	8	5	15	2	5	4

For clarity, according to the data of Table 9 and Table 10, a histogram is developed, which is shown in Figure 3. It allows the planner to quickly evaluate the progress of each order.

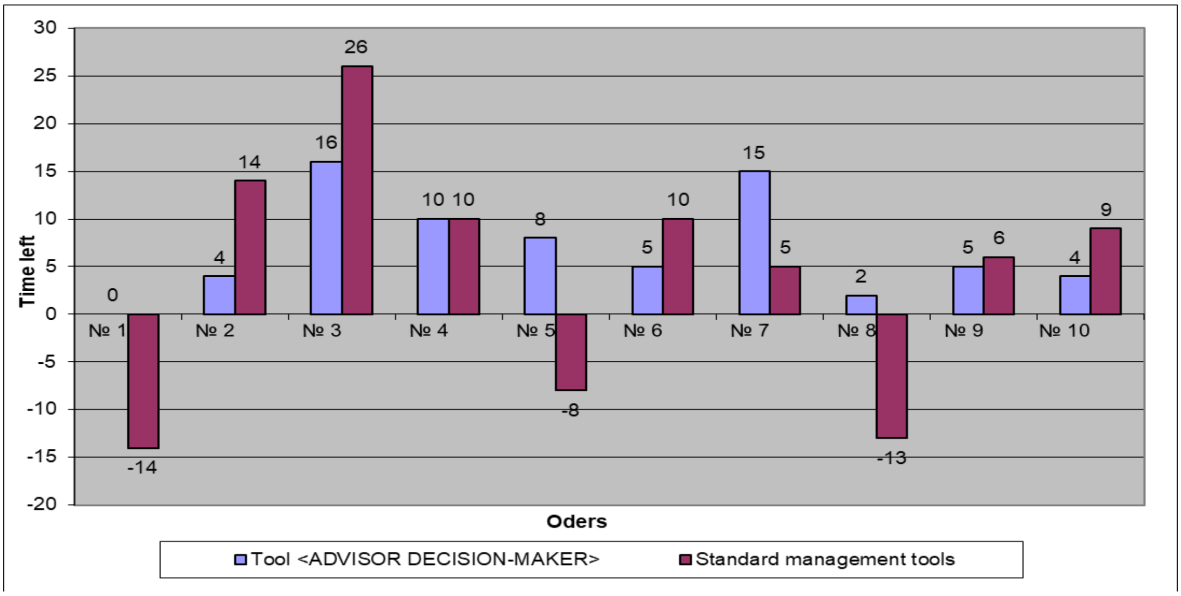

Fig. 3. Time remaining data obtained using tool <ADVISOR DECISION-MAKER>. *Source: Author's research*

Based on the results obtained in accordance with the established conditions the following conclusions can be made about the effectiveness of using tool <ADVISOR DECISION-MAKER>. Firstly, the entire group of orders is completed on time. Secondly, this group of orders has a maximum reserve of the remaining time, which can be used by the scheduler to expand the portfolio of orders.

Thus, the task was solved for the case of printing orders competing for common resources and having different parameters for their implementation. The DM using the software tool <ADVISOR DECISION-MAKER> has found the <Solution> in the form of optimal sequences of passage of competitive points by all orders. The implementation of such a Decision ensures the fulfillment of all orders within the deadlines established by the contracts.

The result of the work is a model and technology to find priorities for the implementation of end-to-end BP with restrictions on the available shared resources, taking into account causal relationships between the actions of the business process and the possibility of obtaining such dependencies.
They enable the DM to find the sequence of implementation of end-to-end BP, not only at the initial stage of their formation but also to change their set by including a new process at various stages of the life cycle of project implementation. Finding the required <Solution> is carried out both in automatic and in combined mode with the participation of the DM [18].
The main difference of the proposed model and technology is the formation of business process initiation (launch) sequences, which is carried out with their sequential fixing at the 1st, 2nd, 3rd, and 4th competitive points until the desired result is obtained.

Their advantage is the implementation of the process of finding such sequences using the criteria of the remaining time and delay time for each business process, which satisfy the DM imposed restrictions on all orders. As a drawback, it should be noted the requirement of preliminary familiarization of the DM with the features and capabilities of the software tool <ADVISOR DECISION-MAKER>. It is used to implement a combined mode of finding the required sequence of access for a set of end-to-end BP to resources common to them, with their obligatory implementation within the deadlines established by the contracts. The model and technology can be applied to various subject areas in which the tasks of planning and operational management of end-to-end BP of a product release or the provision of relevant services to various users are realized and it determines the need for their further development.

Impact
The impact on the economic and social components of the "green economy" by the proposed model and technology is considered in direct proportion to the improvement of management activities of the staff

of a printing company or corporation. Effective management of such complex organizational objects depends first of all on taking into account many interrelated factors affecting the efficiency of their activities. At the same time, such enterprises can execute both periodic and non-periodic orders. Their execution by interconnected BP is implemented by various sequences of actions. Typically, such processes compete for shared resources at various stages of the order fulfillment life cycle. Many departments, services and production units take part in the execution of orders. The order life cycle planning and regulation is directly performed by the planning department of the enterprise. The employees of the planning department introduce the next order into the plan for execution only when the correctness of its preparation and the availability of equipment and supplies has been confirmed.

The planning department defines the business process for completing an order, including its time schedule. The timeline indicates when each order stage will be executed. When a new order appears, the employee of the department faces the difficult task of determining the possibility of its implementation along with other executed orders. The decision depends on many factors. Among them are the availability of supplies, the condition of the required equipment, the availability of human resources as well as time constraints for both ongoing and new orders. The scheduler can determine the sequence of work that will be carried out on equipment (it is possible to combine some work with another similar order to save materials and preparation time). Therefore, the DM must plan, monitor, and manage the status of all executed orders of the printing industry. To fulfill orders within the time limits established by the contracts, he needs real-time information about the condition of the equipment, availability and sufficiency of materials and human resources. Since the DM controls the execution of all active orders at the enterprise, he needs to consider any detail that may become an obstacle to their fulfillment. The DM may directly change any priority (fixing the priority) of launching orders at the corresponding competitive point. The priority fixed by the DM at any competitive point cannot be automatically changed. Only the DM can change or delete the established priority. This is made so that the decision maker could change the priority of the orders at a competitive point, depending on the real-time conditions of the execution of a particular order. In particular, the manual priority change can be applied in case of incidents such as equipment failure, lack of materials, launching of a new order, etc.

Finding the required priority for orders launching at all competitive points is carried out by the DM using the developed software with four runs. If a sequence of priorities that satisfies the conditions for the remaining time was found during the current run, then it is considered optimal. At the following competitive points, the decision maker may continue using this <Solution> or search for other options that would satisfy the newly emerged conditions. Therefore, the advantage of using the developed software is that the DM can adjust the BP to the real-time conditions and restrictions that cannot be foreseen during planning. Moreover, the software set in “just in time” mode automatically adjusts previously obtained results based on modified existing or newly emerged conditions for launching orders. Those results are then used for subsequent analysis and the best option selection.

The main criterion for managing order fulfillment processes is to minimize the waiting time for orders to access shared resources. Untimely execution of one or another end-to-end business process/order leads to significant monetary losses. This fact directly affects the basic economic indicators of the enterprise. Therefore, the model, technology, and software tool <ADVISOR DECISION-MAKER> to be used by planners (DMs) will allow them to find optimal solutions that ensure the execution of orders on time, which directly improves the economic component of the "green economy". The impact of the obtained scientific results, namely, the proposed model and technology for defining the priorities of shared resources access is determined by the complexity of the planning and management of irregular, interconnected end-to-end BP. Existing methods, models and algorithms make it possible to solve main classes of tasks of calendar planning. However, it is difficult to implement them during the management of end-to-end BPs. Therefore, the use of the proposed model and technology and the software tool < ADVISOR DECISION-MAKER > allows the planner to find the optimal <Solution> for real-time management of multiple orders running simultaneously. The process of obtaining such decisions by the DM is considered on the example of determining the priorities of launching 3 printing orders competing for shared resources. The optimal launch priorities were found in accordance with the terms of the contracts. On-time fulfillment of all orders allows to improve the economic and social components of the enterprise, its level of innovation, stability and competitive ability in a dynamically changing market. Thus, this paper attempts to fulfill the research in improving the commercialization of enterprises in the field of Economics and Business.

Conclusions
The general purpose of the article is devoted to the problem of the commercialization of research by using literature studies of existing approaches - environmental, economic and social models for the implementation of the elements of the main components of the "green economy". A harmonious combination of them makes it possible to obtain results that improve the social relations of both producers and consumers of goods and services. The implementation of these components is carried out by various projects. The project is carried out by irregular end-to-end BP competing for common resources in the process of their implementation. The impact on the components of the "green economy" is realized by the proposed model and technology. A decision is being formed on finding the optimal sequence of access for end-to-end BP to shared resources, with restrictions on the time they take to complete. The practical significance of the developed model and technology was conducted by the decision maker using the developed software tool <ADVISOR DECISION-MAKER>. It provides calculations on the necessary parameters for the implementation of projects and the determination of their priorities with subsequent adjustment.

Conflict of interest
There are no conflicts to declare.

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ECO-MANAGEMENT OF ORGANIZATIONS WITHIN THE GREEN ECONOMY SYSTEM

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Abstract
The article examines the significance and role of eco-management in the system of green economy as it is connected with the need to develop new scientific and methodological approaches to managerial decision-making aimed at ensuring resource-oriented production and economic activities of an organization. The purpose of the research is to develop management technologies for eco-management to build a green economy. The eco-management technologies are studied in the following areas: 1) an analysis and evaluation of statistical observations on economic development trends and identification of issues in resource conservation, 2) justification of the need for a new approach to managing organizations, namely considering an environmental component in the decision-making process, 3) the choice of resource-saving measures in terms of a limited financial budget, 4) algorithmic implementation of environmental management components as an important component of an organization's competitive strategy.
The methodical approach to the choice of environmental measures and criteria of resource utilization completeness is suggested. This allows forming the information space as a basis for making management decisions in the field of ecological safety of industrial organizations. During the last decade, the main trends of economic development have confirmed the importance of resource efficiency as far as economic and environmental aspects, which has allowed to determine the impact of research results on the economy and the environment from the standpoint of sustainable development. To this end, practical recommendations for reusing industrial waste in the production activities of companies have been provided. Within the established system of principles, criteria, and factors of rational and efficient use of resources in the conditions of modern economy, the issues of identifying and revealing the features in the development of branch organizations within the mechanism of their resource efficiency have proved to be crucial and of paramount importance.

Keywords
green economy, environmental management, sustainable development, efficiency, resource conservation, environmental responsibility

Introduction

Researchers of possible development strategies for the green economy [1,2] point out that developing a proper strategy is one of the important tools for ensuring the sustainable development of any country. Fatoki has explored the impact of green entrepreneurial orientation (GEO) on sustainable performance (SP) in the context of the hospitality sector [2]. When explaining the role of the green economy in sustainable development, as exemplified by EU member states, researchers [3] conclude that the analysis of different green concepts has historically been linked to a broader discussion of the relationship between sustainable development and the environment. The researchers point out that the issues of resource conservation and resource efficiency under the green economy paradigm are promising and extremely important [4].

The analytical data and statistical observations show that the resource potential is in short supply. According to 2017, in terms of green economy, the world leaders are Sweden (1st place), Switzerland (2nd place), Iceland (3rd place), Norway (4th place), and Finland (5th place). The maximum growth of the green economy index for the period 2015 to 2017 was observed in countries such as China (+15.2), Switzerland (+12.8), and Canada (+10.1) [5]. The development of a wide range of environmentally friendly technologies is expected in the near future (Table 1).

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Table 1. Prospects for the world development of the Green Technology Market in 2016-2025. *Source: [5]*

No	Green Technology Market Segments	2016	2025		Average annual growth rate, 2016 to 2025
		bln euros	bln euros	2025 to 2016	
1	Eco-friendly production, energy storage and distribution (storages, smart grid, etc.)	667	1,164	1.75	6.4
2	Energy efficiency sub-market	837	1,491	1.8	6.6
3	Efficient use of raw materials (including the production of biological substitutes for fossil raw materials)	521	1,048	2.0	8.1
4.	Environmentally-friendly mobility (development of new transport technologies and production of biofuels)	412	988	2.4	10.2
5	Circular economy (waste management)	110	210	1.9	7.4
6	Environmentally sustainable water management (including various aspects of waste management)	667	1,001	1.5	4.6
	Total	3,214	5,902	1.8	6.9

The components of the green technology market cover specific segments and aim at reducing the negative impact on the environment by cutting down the amount of consumed resources, reducing the amount of waste with a goal of full cyclical return of waste to production through deep processing, introducing mechanisms and principles to the production process that display their effectiveness in nature., enhancing the energy efficiency of production and everyday life and improving the properties of materials in terms of environmental safety.

Since 2018, the Global Green Economy Index (GGEI) has been measuring green economy indicators in 130 countries. The paths to green economic growth vary greatly between countries. In terms of the green economy index, the world's leading countries did not change in 2018, but new countries emerged as far as their ranking, such as Ukraine (121st place), Moldova (120th place), and Serbia (115th place). In recent years, fast growing countries have tended to put an increased focus on environmental technologies [6].

The implementation of green technologies is conjugated with expenditures. Environmental expenditures in European countries are accounted in accordance with the SERA-2000 classifier based on the data obtained from enterprises and organizations engaged in environmental protection activities in various sectors of the economy, from households, authorities, and government agencies. In 2018, EU member states spent € 297 billion on environmental protection that made up 1.9% of the gross domestic product [7]. The highest growth rate of expenditures on environmental protection activities of EU member states (Fig. 1) was observed in 2017 when such expenditures accounted for € 289 billion representing 1.955% of the gross domestic product [7].

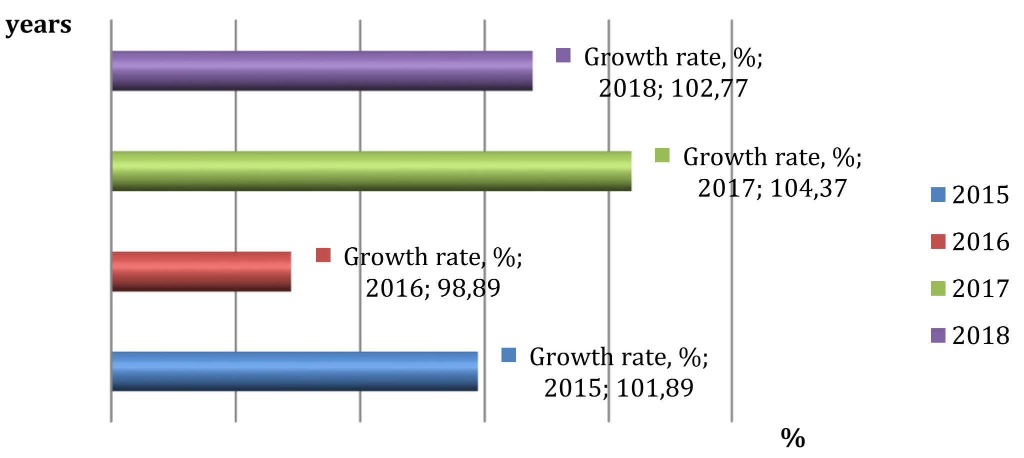

Fig. 1. Comparative dynamics for environmental expenditures. *Source: [7]*

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EU countries have endorsed a joint program for transition to a low carbon economy by 2050. The program sets out the objectives for reducing carbon dioxide emissions by sectors, by both 2030 and 2050 (40-44% and 79-82%, respectively). A number of the measures required to achieve these, and other long-term goals are listed. Such measures include cutting fuel costs (by € 175-320 bln per year) and reducing dependence on energy exports. To increase energy efficiency of the EU economy by 20% by 2020, the following objectives have been determined: to reduce the fixed emission limit within which allowances are allocated and to give access to the market of allowances for sectors that have not previously participated in the tender. The need for these changes is due to the impact of the economic crisis, the fall in the carbon price without a real increase in energy efficiency [7]. For comparison, the growth rate of environmental spending in Ukraine comprised 111.87% in 2015, 132.65% in 2016, 96.92% in 2017 and 106.03% in 2018. That is, in recent years there has been a decrease in the total value of environmental expenditures [8].

When assessing the environmental security of differentiated territories, the experts [9] suggest applying a methodological approach to a comprehensive statistical study of the environmental security of differentiated territories. The approach is based on a method of comprehensive assessment of the environmental security level as a result of the mutual influence of industrial, agricultural, and environmental activities on environmental innovations.

According to the research results [10,11], the scientists formulated the conditions required for establishing a green economy: the adoption and dissemination of sustainable development ideas at different levels of the economic system, the formation of models for economic development with priority to environmental needs, the unification of society on the basis of environmental and humanistic values, and the formation of the rule of law and civil society with the ability to protect human rights and preserve the biosphere. The transition to sustainable development should take place on company, regional, national, and international levels. It is important to combine the interests of an organization with the policy and goals set at a higher level. The researchers [12] presented the current practices and behaviour of companies towards environmental management in the selected industrial sector in the Czech Republic. The authors identified three levels of the environmental management system — legal, basic and mature.

In the face of the global environmental crisis the scientific community emphasizes - there is an urgent need to apply a fundamentally new approach to managing organizations, namely, to consider the environmental factor when making a decision. From this point of view, the most progressive organization management schemes are offered by the European Commission (Environmental Management and Audit Scheme, EMAS) and the International Organization for Standardization (ISO 14001: 2004) [13]. They regulate requirements for the environmental management system (EMS) designed to effectively manage the environmental aspects of company's operations, products and services.

In environmental management, the economic entity operates in human-nature relationships. The closest contact between economic entities with an environmental management system arises when implementing regional policies and programs. Regional resource conservation policy sets common priorities and value orientation for sustainable development of the region [14]. The need for mutual harmonization of requirements in the field of resource conservation with an organization's capabilities causes the establishment of new functional relationships with the systems of environmental management of organizations. According to research that includes World Bank statistics, one-third of all products in the world will eventually not be consumed and go to waste. Unlike in EU member states, in Ukraine, industrial waste increases annually by 14%, which is higher than the consumption rate. More than 40% of all household waste is represented by packaging. As for the industrial enterprises, the production industries are leading in the amount of waste (30 to 95% of their raw materials are not utilized). However, the landfill remains the most common site for disposal of industrial waste materials in Ukraine [15].

To compete successfully in the global market, organizations need to follow green standards including the use of secondary material resources. Reasonable secondary material resources management convincingly proves ecological and economic efficiency. Thus, Greece has introduced waste lubricant oil (WLO) management systems and pushed a number of Greek factories into cutting off the import of raw materials as the amount of WLO is sufficient to meet production needs [16]. Italy and Spain have implemented wastewater treatment projects for textile and leather factories for further use of the wastewater in agricultural and other businesses. These technologies have reduced the overall consumption of water factories by 40%, as well as the load on water resources for industry; they are also able to increase the availability of drinking water in some areas [17].

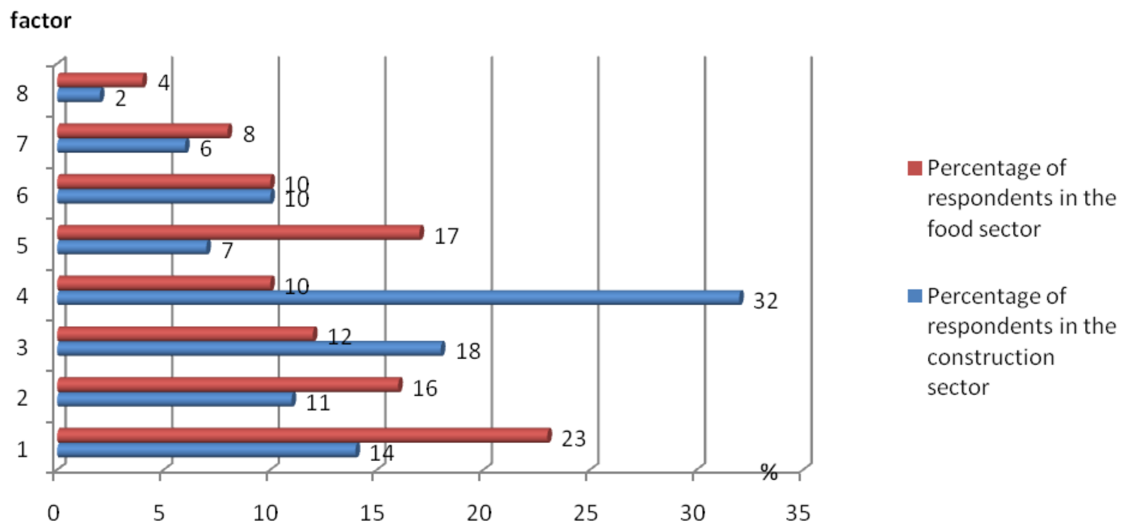
Methods

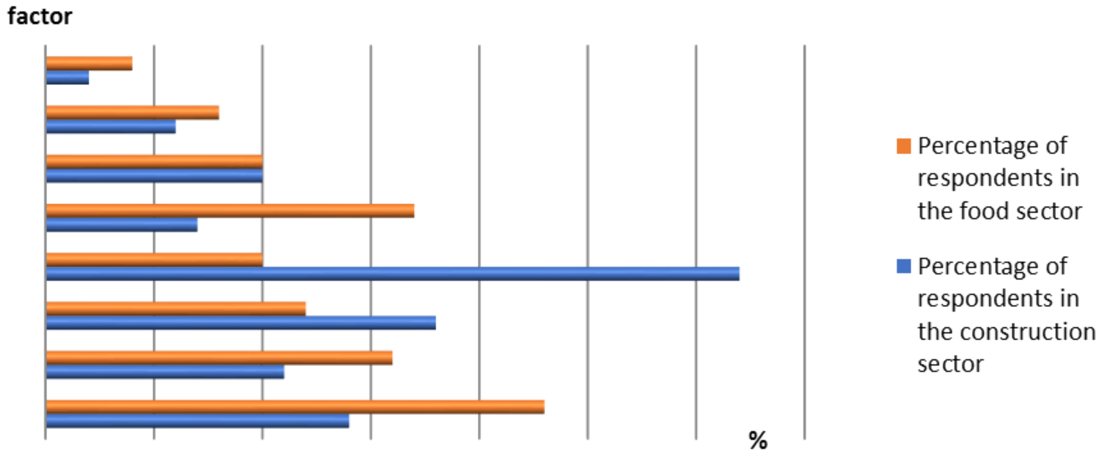
The authors used benchmarking techniques to assess the dynamics of environmental costs for organizations in EU member states and the prospects for the development of the green technology market in the world for 2015-2018. This allowed confirming the relevance of the study and identifying barriers to the green economy development. Using the expert method and questionnaire, the authors have identified the prerequisites for implementing environmental management in Ukrainian industrial companies. The survey was conducted for 40 large and medium-sized industrial companies (50% of firms from the construction sector and 50% of enterprises from the food sector) covering the period from September 2019 to January 2020. The authors controlled such variables as resource consumption by a company (in total MI numbers), number of resource-saving measures, financial resources spent on the event, and the total amount of the environmental budget.

The authors find that the algorithm for selecting resource-saving measures within the organization's environmental management with a limited budget will maximize its impact. An empirical study was based on a set of data on industrial enterprises for the period from September 2019 to January 2020. An expert survey procedure was chosen to implement the algorithm for selecting resource-saving measures of the organization. For this purpose, two expert groups were formed, each of which included enterprise specialists and research staff. Each group was composed of 15 persons. Furthermore, the companies were ranked by level of waste using the waste coefficient as a criterion of completeness.

Results and discussion

Environmental responsibility of business plays an important role in shaping and maintaining the reputation of organizations. To determine the most important prerequisites for implementing environmental management in companies, the researchers surveyed 40 large and medium-sized industrial companies (50% of firms from the construction sector and 50% of organizations from the food sector). The survey was conducted among top and middle level managers. The empirical data obtained during the study indicate that the need for environmental management in companies is driven by the effect produced by such factors (Fig. 2).





Factors: 1. Formation of legal and organizational conditions for rational use of nature. 2. The environmental degradation. 3. Creation of scientific and technical potential for transforming to an economy based on nature conservation. 4. Growth of production capacities with respect to the needs of new technologies. 5. Exacerbation of the environmental impact of companies. 6. Change in the orientation of social production. 7. Minimization of production waste. 8. Arrangement of the production accounting system to reflect the value of natural resources.

Fig. 2. Main prerequisites for implementing environmental management in industrial companies. *Source: Author's*

The Environmental Management System (EMS) is a subsystem of an organization's management system, which operates on the basis of ISO series of standards. International standard ISO 14001: 2004 is based on the Plan-Act-Analyze-Improve methodology. According to the international standard ISO 14001: 2004, an organization must identify the environmental aspects they can control and influence. The head of the organization is responsible for the EMS boundaries within the overall organization management. The boundary can be outlined by the main types of business activities, products and production sites. This choice is based on the following criteria: materiality of environmental aspects; possible application of requirements stated in ISO 14001: 2004; and stakeholder requirements.

The objects of the EMS in the company are represented by products and services; functions (processes) and activities related to these products and services; equipment and various systems (water and power supply, treatment plants, ventilation, etc.); units related to these products, services and equipment. Implementation of environmental management components as an important element of an organization's competitive strategy includes the following main elements such as:

- assessment of the current management system for identifying reserves to increase the competitive advantage of the organization through environmental management
- assessment of the feasibility of implementing an EMS at a particular company in the given period of its life cycle
- introduction of environmental management elements as factors used to create competitive advantage of the organization
- monitoring of competitive advantages created by the environmental management system

One of the EMS strategies is the development and implementation of production tasks in the direction of resource supply with minimal negative impact on the environment. B. and D. Lewicka explore the components of environmental management systems (EMS) and note their strong impact not only on the environment but also on the company image and its financial results [18].

Resource management tools comprise budgeting; formation and adjustment of the regulatory framework (by price, by components of the main types of resources); control of resource supply processes; stimulation of resource saving production by all participants at every stage of the manufacturing process. The implementation of resource-saving measures is complicated by the scarcity of financial resources. Therefore, it is necessary to select measures which will allow achieving maximum effect in terms of a limited budget. This requires relevant information. The authors [19, 20] classify information sources and emphasize the use of reliable data in making management decisions at the enterprise level. The authors suggest selecting resource-saving measures based on two parameters such as maximizing resource savings and minimizing financial costs. Resource maximization is estimated in total MI numbers, whereas minimization of financial expenses is expressed in terms of monetary units. The solution method is integer linear programming: 1 (the measure is to be implemented), 0 (the measure is not to be implemented). When solving the problem, it is assumed that the jth measure corresponds to δ_j(j = 1, ..., n). Mathematical description of the problem of choosing a priority measure in solving the resource conservation issue is as follows [21]:

$$\max L = \sum_{j=1}^{n} c_j \delta_j \tag{1}$$

$$\begin{cases} \sum_{j=1}^{n} a_{ij}\delta_j \le b_i (i = 1,\dots,n), \\ \sum_{j=1}^{n} \delta_j \le n \end{cases} \tag{2}$$

Where L — total reduction in the organization's resource consumption (in MI aggregate numbers); c_j — reduction in the organization's resource consumption (in MI aggregate numbers) in undertaking the δ_j measure; n — number of resource-saving activities; a_{ij} — financial resources spent on undertaking the δ_j measure; b_i — total amount of the environmental budget.

The algorithm for choosing resource-saving measures with a limited financial budget is presented in Fig. 3, where Ej — effectiveness of the measure undertaken.

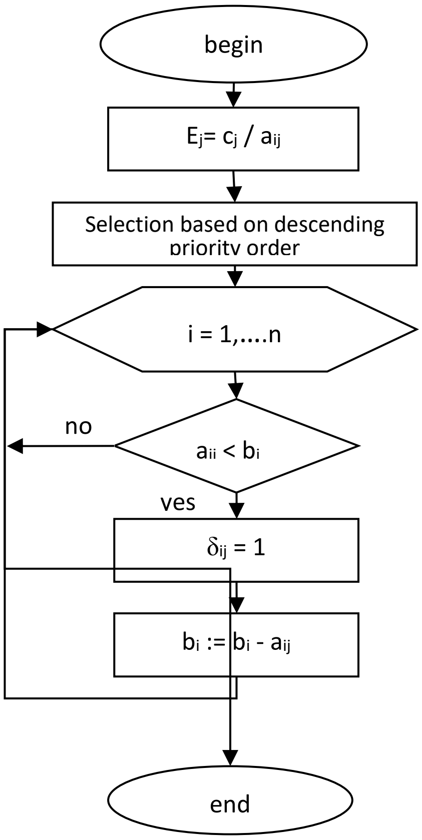


Fig. 3. An algorithm for selecting resource-saving measures within the environmental management of the organization.
Source: Author's

Thus, solving the problem of integer programming with Boolean variables allows identifying the most significant environmental measures considering the availability of limited financial resources of the company.

To implement the algorithm for selecting resource-saving measures within the environmental management of the organization, an expert survey procedure is chosen. The expert survey procedure includes organizational, methodological and analytical steps. At the organizational stage, a working group is formed. Expert competence is assessed through questioning, analysing the level of referencing (the number of references to the specialist's work) and using self-assessment sheets. The degree of suitability of a particular expert for the questionnaire is determined by the competence coefficient:

$$K_a = \Sigma V_{ij} / \Sigma V_j \quad (3)$$

Where K_a – reliability factor of the questionnaires; V_{ij} – weight of the j^{th} gradation (emphasized by the expert who is being evaluated) and the i^{th} characteristic (in points); V_j – the maximum weight of the j^{th} characteristic (in points).

In the process of self-assessment, each expert determines his/her education level using a ten-point grading scale which contains indicators characterizing the degree of the expert's participation in the development of the issue under study. Based on the self-assessment, the expert's competence is calculated:

$$Kc = \Sigma k / \Sigma n \quad (4)$$

Where Kc – the expert's self-esteem competence factor; k – self-assessment (in points) which characterizes the degree of expert's awareness of the k^{th} problem; n – the highest possible self-esteem (10 points).

As a result, two expert groups were formed, taking into account the sphere of business activities. This group included enterprise professionals and researchers. Each group was composed of 15 persons.

At the methodical stage, a problem was formulated, questionnaires were developed, survey period and schedules were set. The degree of concordance of experts' opinions was assessed using the coefficient of concordance. K_{con} (expert group 1) – 0.905, K_{con} (expert group 2) – 0.852. The statistical significance of the coefficient of concordance was verified by the Person criterion. At the analytical stage, priority directions were outlined to solve the problems of resource conservation for industrial enterprises (large and medium-sized) of the food and construction industries. These directions were clustered as follows: 1) technological; 2) environmental; 3) marketing; 4) organizational (Tables 2-5).

Table 2. Ranking results for technological measures. *Source: Author's*

No	Measure	Company ranking by industry			
		industrial construction companies		food engineering companies	
		large	medium-sized	large	medium-sized
1	Application of low-waste and non-waste technologies	6.25	5.12	6.12	7.00
2	Repair and replacement of obsolete equipment	2.1	2.2	3.01	4.14
3	Increasing the mechanization and automation level of production	3.05	3.01	5.1	3.02
4	Development of project documentation for the use of advanced technologies	4.2	4.41	2.09	1.4
5	Quality control of raw materials	6.98	6.79	7.00	6.14
6	Arrangement of waste collection, sorting and utilization	5.11	6.08	4.1	5.02
7	Other	1.1	1.12	1.58	2.34

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Technological measures are aimed at reducing waste and loss of materials. The activities of this group take place at the stage of production. An expert analysis has revealed that the experts select the use of low-waste and waste-free technologies and quality control of raw materials taking into account the peculiarities of activities, duration of the production cycle, and the most significant technological measures in the direction of resource conservation. The processes of arranging the collection, sorting and use of waste and developing project documentation for the use of advanced technologies are quite significant.

Table 3. Ranking results for ecological measures. *Source: Author's*

No	Measure	Company ranking by industry			
		industrial construction companies		food engineering companies	
		large	medium-sized	large	medium-sized
1	Assessment of the harmful effects of the organization's production on the environment	3.41	3.03	3.04	3.12
2	Reflection on the interconnection of the main production and environmental activities of an enterprise in the policy	2.14	4.01	4.32	4.012
3	Use of eco-labels	5.00	4.958	5.00	4.587
4	Preparation of proactive environmental reporting (green reporting)	4.14	1.04	2.3	1.02
5	other	1.03	2.21	1.05	2.4

Environmental measures are aimed at maintaining environmental security to ensure sustainable development. An expert analysis has revealed that the most significant environmental measures of organizations in the construction industry are using environmental labelling, reflecting the interconnection of the main production and environmental activities of organizations (for medium-sized businesses) in the policy and preparing proactive environmental reports (for large organizations). The most significant environmental measures of food industry organizations are using eco-labels and reflecting the interconnection of the main production and environmental activities in the company's policy.

Table 4. Ranking results for marketing measures. *Source: Author's*

No	Measure	Company ranking by industry			
		industrial construction companies		food engineering companies	
		large	medium-sized	large	medium-sized
1	Identifying the most profitable suppliers in terms of their geographical location	1.02	1.01	5.45	4.13
2	Choosing the best vehicles for deliveries	3.2	2.13	3.00	3.12
3	Constantly specifying contract work details and revising the list of suppliers considering their stable position in the market and reliability in fulfilling their obligations	6.00	6.00	2.05	2.14
4	Expanding methods of interaction with customers based on their accurate fulfilment of the agreed delivery conditions regarding assortment, amount, terms and address.	5.01	5.00	5.897	5.98
5	Developing the most rational schemes and routes for cargo transportation	4.23	4.27	4.17	5.03
6	Other	2.1	3.12	1.02	1.1

Marketing activities are aimed at finding and attracting reliable partners. An expert analysis has revealed that the most significant environmental measures taken by organizations of the construction industry are as follows: constantly refining contract work details and revising the list of suppliers considering their stable position in the market, reliability in fulfilling obligations and expanding methods of interaction with customers on the basis of the most accurate and agree terms of delivery. For food industry organizations, it is the development of the most rational schemes and routes of cargo transportation and expansion of methods to interact with customers.

Table 5. Results of organizational measures ranking. *Source: Author's*

No	Measure	Company ranking by industry			
		industrial construction companies		food engineering companies	
		large	medium-sized	large	medium-sized
1	Optimizing the organizational structure of resource management and distributing responsibilities	1.01	1.05	2.02	1.01
2	Developing normative-technical and organizational-methodological base (standards)	5.98	5.00	6.89	7.00
3	Operational control over the targeted use of human resources	4.01	4.02	3.00	3.04
4	Operational control over the targeted use of logistical resources	5.01	6.03	4.03	6.125
5	Production planning, including the development of network schedules, calendar plans, work schedules, resource schedules;	7.00	6.98	5.985	4.789
6	Staff training, internships and advanced training	3.06	3.21	5.02	5.04
7	Other	2.2	2.3	1.01	2.2

Organizational activities are aimed at improving the production organization and planning with a view towards the rational use of resources. They are to develop a comprehensive resource management system for the company. According to the experts, the most significant environmental measures of industrial construction companies are as follows: production planning, development of regulatory, technical and organizational, and methodological base (standards), operational control over the targeted use of material and technical resources. The following measures are defined for food industry organizations: development of normative-technical and organizational-methodological base, production planning, and personnel training.

Consistent implementation of the studied measures provides an opportunity to evaluate the effectiveness for the organization as a whole. For this purpose, it is advisable to use a system of targets, including the rate of resource consumption reductions, the rate of harmful emission reductions, the rate of material resource utilization, the rate of production volume growth and the product range expansion based on cost savings.

When developing a resource conservation policy, an organization should identify the key factors that affect the effectiveness of the methods used and the degree to which the targets are met within the organization's resource-oriented activities. To this end, on-going and strategic analyses of the activities should be carried out. A factor that has a direct impact on the efficiency of an organization's resource conservation is industrial waste processing and recycling. In EU countries, considerable attention is paid to the promotion of products made using recycled materials. In terms of profitability, such production may be inferior to environmental value. Considering the complexity of the connection between the functional elements of the eco-economic system and the material and raw-material flows, the place of waste in the reproduction system has been determined (Fig. 4). This made it possible to justify possible directions of industrial waste utilization in the organization and to evaluate their impact on the results of economic activity.

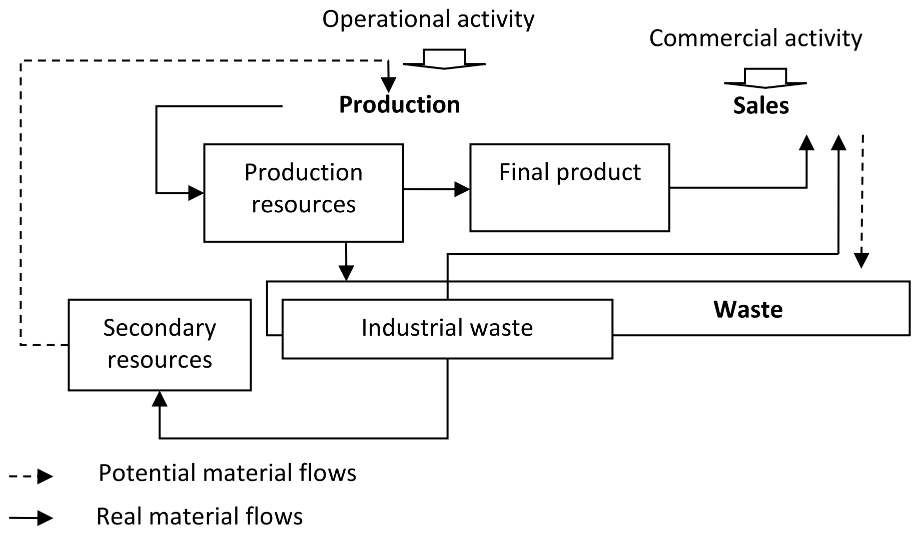

Fig. 4. Waste positioning in the organization's reproduction system. *Source: Author's*

The key elements of a waste management strategy are the prevention of waste accumulation or its minimization. Reuse, disposal or demolition of wastes is only intended to be used in cases in which there are no other alternatives available. Thus, the use and implementation of methods for preventing industrial waste accumulation is a paramount principle of the waste management strategy in the environmental management system.

The criterion of completeness for resource use is the coefficient of non-waste:

$$K_{nw} = f \cdot Km \cdot Ke \cdot Ka \tag{5}$$

Where f — empirical coefficient of proportionality; Km — coefficient of material resource use; Ke — coefficient of completeness of energy resource use; Ka — coefficient of conformity of production to energy requirements.

Grouping of surveyed organizations by the waste rate is represented in Table 6.

Table 6. Company ranking by the level of profitability. *Source: Author's*

groups	Km value	Group Name	Number of companies surveyed by industry and size,%			
			industrial construction companies		food engineering companies	
			large	medium-sized	large	medium-sized
I	Кm ≤ 0-0,51	waste	22	18	18	29
II	Km ≤ 0,81 - 0,9	low-waste	64	71	73	64
III	Кm > 0,9	waste-free	14	11	9	7

The implementation of EMS in the organization improves its management, sustainability (through improving the quality of manufactured products; increasing the competitiveness level; reducing costs associated with the environmental impact of the organization; and increasing investment) and mobility (through improving production efficiency and products being recognized at the international level and in the world market). These benefits can be attributed to the systemic advantages obtained as a result of EMS implementation.

We agree with the research results provided by Chorna, Filipishyna et al, regarding the importance of analytical support for the management of economic and environmental security of organizations [22]. The effectiveness of managing the environmental and economic security of an organization depends on the starting points of the ecological and economic analysis. At the same time, the results of such analysis are important in the field of environmental management for the quality of management and alternative directions of the resource conservation strategy. Anishchenko et al., [23] present the results of an environmental safety analysis of a company through waste management. The criteria that can be used to recognize waste as an economic resource are identified. These criteria are the basis for a new understanding of such an economic concept and the basis for shaping the behaviour of economic agents in waste management. We believe that the criteria they offer have a significant impact on the formation of a waste accounting system and waste management operations. Novikovas and Stankevičius define the elements of environmental safety, namely, waste management, which is characterized as a complex phenomenon that includes administrative, functional, political, and technological aspects, along with the aspects of infrastructure [24].

The research has also been conducted towards extending the results of Kochańska, Adamkiewicz, and Bertozo, who analyze the possibility of using fish waste to increase the profitability of fish processing enterprises [25].

Bombiak [26] notes that the modern concept of business management includes conscious activity focused not only on financial profit and economic aspects but also on social and environmental interests. At the same time, the author [26] emphasizes, and we agree, that eco-oriented management is carried out exclusively by employees with a positive attitude towards the environment, environmentally friendly competences and who take responsibility for the environmental consequences of their actions. Thus, the environmental management system of the company becomes effective in compliance with the principles of environmental corporate responsibility and environmental awareness of employees and managers, which are the keys to the sustainable development of the organization.

The study of the theoretical aspects and practical recommendations of these authors suggests that they have deepened the theoretical foundations and practical tools of environmental management in organizational management systems. However, it requires innovative approaches to analytically ensure the environmental management of the organization based on compliance with the objectives of the quality management level and alternative areas of the resource conservation strategy which determined the choice of research topic.
Working in line with researches of these scientists, the authors have expanded the use of eco-management tools and found that the algorithm for selecting resource-saving measures within the organization's environmental management with a limited budget will maximize its impact.

Impact

Ensuring company development in a green economy can be improved by implementing EMS in the company. Eco management provides the organization with:

- increased level of management culture and proper activities
- ecological quality of products (services) in the green economy system
- increased competitiveness of products by taking into account the environmental component
- sustainable and enhanced company reputation towards ensuring environmental responsibility of the business
- sustainable development of the organization.

Application of the proposed algorithm for selecting resource-saving measures in the framework of environmental management provides an opportunity to analyze the issues of rationality, resource conservation and resource efficiency of production and technological units at the scientific and practical level, regardless of the forms and methods of production and economic activities.

The proposed environmental liability measures can bring real value in financial terms. This is possible through a waste management strategy at the business unit level to prevent their generation or minimization of waste. At medium-sized enterprises in the construction sector, the cost of recycling construction materials (including safety and regulations) comprised more than $ 15,000 per operating cycle. For medium-sized enterprises in the food industry (including safety and regulatory standards) it accounted for more than $ 7,000 per operating cycle. Therefore, at the country's level of economy, this is an element of waste management strategy in the environmental management system.

The results of this study are relevant to improving and modernizing a complex economy model of resource-saving green type, in particular, at the level of a business entity acting in the real sector of the actor economy. Since the International Standard ISO 14001: 2004 requires that companies identify environmental aspects of their activity, the authors offer management tools for resource management such as budgeting; control over the resource supply process; stimulation of resource saving policies by all participants at all stages of the production process. This approach should be based on a consistent account of factors, criteria and principles of resource conservation at all levels of management, purposeful improvement of existing management structures, and implementation of environmental management.

The scientific novelty of the research lies in improving the methodological tools of the company's environmental management, which are based on a comprehensive account of cause-and-effect relationships between changes in the environment and internal resources and management capabilities of the business unit. Such improvement is suggested in the context of continuous improvement of eco-management systems in the company, which is possible by extending the boundaries of its scope and, consequently, the degree of influence of the organization on the consequences of its activities and the environment as a whole. The eco-management toolkit has been improved through the use of integer linear programming to evaluate the level of resource efficiency of an individual business unit systematically and quantitatively. This makes it possible to further develop evidence-based recommendations for improving eco-management.

Conclusions

In the last decade, there has been an extensive environmental management trend. The environmental management system is the result of many years of experience and experiments in the management system of organizations, institutes and professional communities in a number of countries where the public authorities have been instrumental in this process. The introduction of EMS in businesses has a positive impact on the health and ecological culture of employees and the entire population across the territories adjacent to the organization.

EMS examines the production process in detail from the point of view of the negative impact on the environment through industrial waste management. To effectively address the industrial waste management issues, organizations are recommended to use the techniques focused on reducing environmental expenditures in the structure of production cost and motivating business entities to adopt the policy of resource conservation and waste treatment.

Based on the research results, the main prerequisites for implementing environmental management in industrial organizations have been identified. The mechanism for introducing environmental management components has been suggested as an important constituent of an organization's competitive strategy. The algorithm of selecting resource-saving measures within the environmental management of the organization has been presented. On the basis of the given algorithm, nature conservation measures within the construction and food industry organizations have been ranked. Considering the complexity of the connection between the functional elements of the eco-economic system and the material and raw-material flows, the place of waste in the reproduction system has been determined. This allowed justifying possible directions of industrial waste utilization in the organization and evaluating their impact on the results of economic activities.

Ensuring the development of a green economy when selecting the necessary tools requires considering the possibility to save material costs through returning industrial waste to production. Such measures influence the effectiveness of organizations, their social and ecological responsibility and are aimed at ensuring the health and social protection of future generations.

The proposed research findings have practical significance (already in use) in the context of large and medium-sized industry organizations of Ukraine. At the same time, the algorithm for selecting resource-saving technologies can be reproduced for organizations in different industries and used in different geographical locations. Since this research further extends the previous study, it focuses on practical resource-saving technologies in managing organizations. The research complements the experience that looks at management mechanisms related to resource-saving technologies that affect business performance.

Conflict of interest

There are no conflicts to declare.

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