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Research paper

Bioenergy production side-streams availability assessment as decision making driver for sustainable valorisation technologies development. Case study: Bioethanol and biodiesel industries



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ABSTRACT

Recently, biorefineries have emerged globally as an attractive alternative to conventional fuel production, but costs still need to be competitive. Latest policy actions such as the Green Deal or the Circular Economy Action Plan encourage maximising the biomass-to-products value chain through the use of all valuable compounds available in side-streams to the full extent. Side-streams from corn and rapeseed-based biofuels industries represent excellent sources of bioactive compounds and proteins, mainly under-utilised as animal feed without uncovering their full potential at industrial sectors such as food supplement, speciality chemicals, cosmetics, and household products. The main objective of the research conducted is to pave the way for side-streams valorisation technologies upgrading and market penetration by assessing current availability and future production rates of corn oil, thin stillage, rapeseed meal and other biodiesel and bioethanol production side-streams. Through a bibliographic analysis of peer-reviewed articles and grey literature, key information and valuable data are presented. It is possible to conclude that trends in biofuel markets (supported by regional regulations) lead to increased biofuel production, as well as increased availability of the specified side-streams. Corn oil is produced at a rate of 60 million L/year on average in Europe, a total of 1.6 billion L of thin stillage is produced each year, and rapeseed meal is generated at a global rate of 68 million tons per year. Future research to trigger further developments and investments could dive into the types and regional availability of relevant active compounds found in the selected side-streams.

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1. Introduction

Biorefineries (integrated production plants that produce valueadded products and energy using feedstocks such as biomass or biomass-derived) are gaining increasing relevance with several companies emerging in the area. According to Global Industry Analysts, Inc., in 2026 the global market of biorefinery technologies will grow from 506.9 billion $\\mathbb{C}$ in 2020 to 896.7 billion $\\mathbb{C}$ and at a compound annual growth rate (CAGR) of 9.8% for that period (Global Industry Analysts, Inc, 2022). Table 1 provides information on biorefineries that have recently been identified in Europe through several studies by the Bioindustries Consortium (BIC, 2017) and the European Commission-Joint Research Centre (EC-JRC) (Parisi, 2018, 2020). EC-JRC studies consider biorefineries at different Technology Readiness Level, including commercial, demo, pilot, and R&D biorefineries. The information produced through these studies is gathered in the EC-JRC Data-Modelling platform for agroeconomic research, which currently provides information on 2.362 facilities that use biomass as feedstock for product manufacturing.

From the biorefinery landscape (Table 1), special attention is paid to biofuels and bioenergy production, since European Union (EU) legislation trends and strategies are designed to reduce carbon emissions and ensure energy sustainability. In fact, in 2018 biofuels and bioenergy accounted for roughly 15% of the turnover of the EU industrial sectors that are referred to as 'biobased economy' (Porc et al., 2021). That year, the total turnover

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Table	1
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Biorefinery production/Year	2017 (BIC, 2017)	2018 ^a (Parisi, 2018)	2020 (Parisi, 2020)
Pulp and paper	-	507	569
Chemicals	54	363	528
Timber	-	141	491
Biomethane	-	803	379
Liquid biofuels	64	-	339
Starch and sugar	63	-	202
Composites and fibres	-	-	147
Total	224	802	2362
Integrated	25+5	177	240

^aMultiproduct facilities are counted more than once.

in the bio-based economy was 776 billion €, which biofuels and bioenergy corresponds to a total amount of approximately 114 billion € (Porc et al., 2021). To reduce greenhouse gas emissions, biofuels must be produced in a sustainable manner. Thus, the EU has established rigorous sustainability criteria for biofuels and bioliquids. These are provided in the revised Renewable Energy Directive - REDII (EU) 2018/2001, where the promotion and use of energy from renewable sources in the EU are supported by policy measures. This also aligns with the Sustainable Development Goals of the United Nations (SDGs), such as SDG7-Affordable and Clean Energy, SDG9-Industry, Innovation and Infrastructure, and SDG12-Responsible Consumption and Production, and more specifically SDG 12.2 'By 2030, achieve sustainable management and efficient use of natural resources', highlighting sustainability in the private sector. Section 3 dives deeper into the SDGs and how they may affect the availability and valorisation strategies of side-streams.

In this context, there is an emerging interest worldwide for new approaches to the valorisation of side-streams of biotech productions, improving their environmental and economic profile, and ensuring higher sustainability of the bioenergy supply chain. These industrial processes usually produce by-products that are used mostly for energy, animal feed, or other lowvalue purposes. To compete successfully as a sustainable energy source, the extent of biomass utilisation must be maximised through the production of valuable co-products in biorefineries. The current situation at global level points out the need to increase the availability of bioactive compounds and proteins: it is clear then that the next incremental steps towards sustainability would be to utilise all bioactive compounds and proteins from biorefinery side-streams and effluents to the full extent. Co-streams from the corn and rapeseed from biofuel producing industries represent excellent sources of bioactive compounds, currently under-utilised mainly as an animal feed (Makkar, 2012). Their potential is to be used in different industries such as food supplement (rapeseed meal relevant properties for human food supplements are emulsification, foaming, and gelling (Tan et al., 2011), speciality chemicals (used for bioplastics production (Mirpoor et al., 2021)), cosmetics (skin care applications (Rivera et al., 2015)) as well as detergent market (biosurfactants (Konkol et al., 2019)). There have already been several attempts of side-streams valorisation into other value-added applications (e.g., the recovery of corn oil to produce biodiesel, the production of biogas from thin stillage anaerobic digestion, or the treatment of dried distillers' grains with solubles (DDGS) with supercritical CO₂), but this is still far from fully exploiting all the potential within these streams.

In this scenario, where new valorisation processes have to be developed, availability and sustainability of biorefineries sidestreams production is the key aspect since process and technology upgrade is related to a long-lasting, proper supply of the needed resources. An integrated valorisation strongly connected to feedstock supply chains ensures that these biorefineries and new linked value chains remain as environmentally friendly and socially respectful as possible. Producing added value biobased products using these side-streams as feedstock (following the emerging EU paradigms of integrated biorefinery and circular economy) is necessary in order to maximise full biomass-toproducts value along the whole value chain. Also, this would allow one to have competitive production costs of biofuels without any governmental support (Orts and McMahan, 2016).

However, technology developers, policy makers, and investors are not able to find enough and solid information about the availability of these biomass sources when evaluating the possibility of commercially exploiting the aforementioned side-streams valorisation approaches. This fact increases investment risks, hindering the further evolution of the biofuels production industry towards a more consolidated circular bioeconomy.

Currently, publications about side-streams focus more on assessments of their potential as sources of new compounds in the frame of circular economy (Konwar et al., 2018), or outcomes of new valorisation processes development e.g. rhamnolipids production from biodiesel side-streams (Baskaran et al., 2021). However, the side-streams availability assessment exercise has been conducted for the food industry, where a food processing sidestreams inventory for the EU was published in 2020 (Ladakis et al., 2020). Therefore, a thorough analysis of biofuel product side-stream availability seems lacking in the literature, which is very much needed in order to support the further development of the biofuel industry and to avoid lagging behind other biomass-related industries.

The present study attempts to gather information on the availability of the side-streams of interest (corn oil, thin stillage, and rapeseed meal), delving into the composition, quality, and quantity to close this gap. To the best of the authors' knowledge, no systematic analysis has been performed in this biomass subject area to ensure the reproducibility of the valorisation processes to be further developed. In this vein, the following research questions (RQs) are addressed through a systematic literature evaluation and analysis:

• RQ1. How are the SDG and European and North-American policies related to selected side-streams generation and valorisation?

• RQ2. What is the availability of bioethanol side-streams (corn oil and thin stillage)?

• RQ3. What is the availability of biodiesel side-stream (rape-seed meal)?

• RQ4. What is the availability of other side-streams of interest as alternatives to the corn and rapeseed proceeding by-products?

The research presented herein is structured as follows. An overview of the process followed for literature review and analvsis is provided in Section 2. Here, the selected biorefineries (bioethanol and biodiesel production) are presented, together with the selected side-streams and their characterisation. The results are presented and discussed in Section 3 in four steps: (i) brief review of the SDGs and policies and how these interrelate with the side-streams production and valorisation (answer to RQ1); (ii) information on the availability of corn oil and thin stillage (answer to RQ2); (iii) information about the availability of rapeseed meal (answer to RQ3); (iv) availability of other sidestreams of interest as alternatives to subsequent by-products of corn and rapeseed processing for biofuels production (answer to RQ4). Finally, Section 4 summarises the main results, points out the limitations of the present research, and outlines the potential opportunities and prospects for future developments.

One of the most important components and innovation aspect of this research is the analysis of side-streams availability

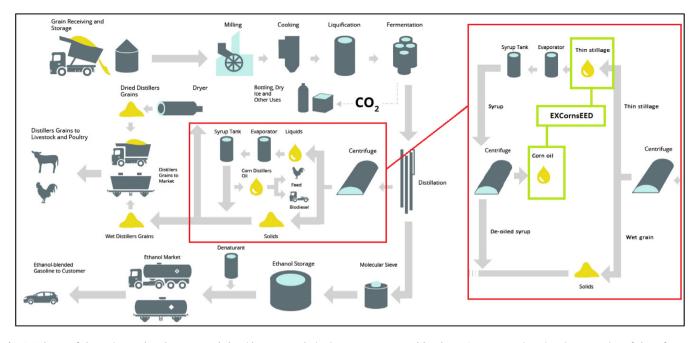


Fig. 1. Scheme of the grain-to-ethanol process and the side-stream valorisation process proposed by the EXCornsEED project. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) *Source:* Own.

information that is scattered through different sources and that in most cases is hard to find or not available. Since these biomass sources are usually considered as by-products/co-products or side-streams/secondary effluents, not much work has been done to quantify them at the country or regional level.

2. Methods

A literature review (Caulley, 2007) was used as the research methodology in this work. This was done first to gain a current understanding of the availability of side-streams. The study was based on input from both scholarly journals and non-academic organisations.

This was decided due to the novelty of the knowledge area (circular bioeconomy), a decision supported by conclusions from Geissdoerfer et al. (2017) concerning research in the circular economy. "The inclusion of non-peer-reviewed articles is appropriate since circular economy is a new area of research and (...) has not been extensively addressed by peer reviewed articles".

On the one hand, the emphasis on peer-reviewed papers ensures scientific integrity. On the other hand, research projects or reports developed by other organisations (such as the European Commission and linked Joint Research Centres) involved in the circular bioeconomy transition and working closely with businesses could reflect current industrial reality and needs regarding side-streams availability, and thus provide additional meaningful insights. In this light, the following data sources have been examined: Science Direct, Web of Science, SAGE, Springer, Taylor & Francis, Google Scholar, Google, European Commission, among other minor sources from industrial associations, project reports, etc. Various strings of keywords were used: (i) "bioethanol" AND "side-stream" OR "side-stream" AND "production" OR "availability"; (ii) "biodiesel" AND "side-stream" OR "side-stream" AND "production" OR "availability"; (iii) the different names of selected side-streams (corn oil, thin stillage and rapeseed meal) were also searched independently next to AND "production" OR "availability". Concerning the selection and analysis process, firstly, works (including peer-reviewed academic journals, conference papers, research reports, postgraduate dissertations,

books, websites, and reports) that were deemed non-relevant for side-stream availability evaluation were discarded based on scanning titles, abstracts, and/or short contents. Then those that dealt directly with or had indirect links with side-streams availability assessment were scrutinised in depth and critically.

The data presented next cover not only Europe but also the United States (13.8 billion gallons of ethanol produced in 2020 (Sönnichsen, 2021b) and 1.72 billion gallons of biodiesel produced in 2019 (Sönnichsen, 2021a)) as this is a relevant market that would need to be evaluated as well.

2.1. Description of selected biorefineries

The research presented herein has been conducted in the framework of the EXCornsEED project, an innovation project devoted to biorefinery side-streams valorisation through a combination of extraction, concentration, and purification technologies. The case study for this project has been Envien Group, based in the region of Central and Eastern Europe (Slovakia, Czech Republic, Hungary, and Croatia, which is one of the largest and most significant groups of companies in such an area) active in the production of biofuels. An example of bioethanol and biodiesel production plants and alternative side-streams valorisation routes proposed in the EXCornsEED project can be found in Figs. 1 and 2.

Grain-to-ethanol production

Dry grinding is the most common method of ethanol production worldwide, which concentrates corn and yeast nutrients in downstream operations. Thin stillage side-stream is a liquid material produced in substantial amounts at bioethanol plants after the centrifugation of thick (whole) stillage. The material is concentrated by evaporation, resulting in a syrup that is used for further production of DDGS. In biorefineries that follow this method, each ton of corn produces approximately 429 L of ethanol, 304 kg of DDGS and CO₂. Crude corn oil can be produced in these plants by extracting the oil from the thin stillage portion of the DDGS production process. In this way, the resulting corn oil is more valuable compared to fodder DDGS, although the volume and lipid content of the DDGS are reduced.

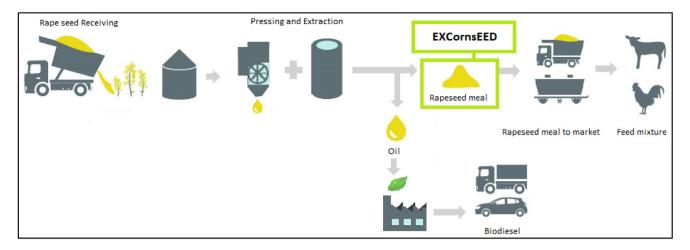


Fig. 2. Scheme of the rapeseed-to-biodiesel process and the side-stream valorisation process proposed by the EXCornsEED project. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The main criterion for the acceptance/ refusal of corn from suppliers is the whole moisture content (max. 14.0 w/w%). Corn starch content is another valuable criterion (min. 62 w/w%). On the basis of the production requirement, the maize is discharged and transported into an operational storage house from which it is directly used in the bioethanol production process. Thin stillage is currently used for DDGS production. The majority of undissolved solids are removed, but thin stillage is rich in proteins and amino acids, carbon sources such as soluble fibres, the rest of starch hydrolysates (dextrin), glycerol, glucose, maltose, and xylose. To co-produce corn oil bioethanol plants integrate a centrifuge-based extraction system into the standard dry mill process. This system separates corn oil from the corn syrup (concentrated stillage) portion that results from fermentation and distillation processes before it is thermally treated in the dryer to DDGS. A scheme of the aforementioned plant can be found in Fig. 1.

Rapeseed-to-biodiesel plant

Biodiesel can be produced by the subsequent pressing and extraction of oil from rape seeds (also known as canola), having rapeseed meal in copious amounts as a by-product after the deoiling process. Non-GMO rapeseed meal is a free-flowing material without sintered pieces over 10 cm. Rapeseed meal is currently used as a feed ingredient for the preparation of feed mixtures for farm animals. It supports the digestion process and contains a balanced proportion of nutrients. A scheme of the aforementioned plant can be found in Fig. 2.

2.2. Biorefinery effluents of interest selection

Corn oil (liquid side-stream of bioethanol production, isolated from corn stillage) is rich in lipophilic bio-active substances such as carotenoids, phytosterols, isoprenoids (squalene), tocopherols, pigments, Omega 3-6-9 and vitamins. The main composition is depicted in Table 2. Corn oil is currently used as an alternative feedstock for biodiesel production, but preliminary studies by ENVIRAL, a. s. found that many compounds present in the stream hamper the efficiency of biodiesel production (acting as 'impurities'), while at the same time its full value as ingredients for high-end applications could bring additional business revenues to the company.

Thin stillage (liquid side-stream of bioethanol production) is a liquid material produced in bioethanol plants in large quantities resulting from centrifugation of heavy stillage and concentrated by evaporation. Most undissolved solids are removed, but thin

Table 2Main composition of selected side-streams.

Source: Di Lena et al. (2020), Lena et al. (2020a) and Rusu et al. (2020).

Monitored parameter	Selected side-streams			
	Corn oil	Thin stillage	Rapeseed meal	
Dry Matter (% w/w)	99.63	7.13	90	
Ash (g/100 g, wet mass basis)	-	0.72	6.27	
Crude Protein (% w/w)	0	1.35–1.55 (13.5–15.5 g/kg)	35	
Crude Fat (g/100 g, wet mass basis)	-	1.87	2.11	
Acid value (mg KOH/g)	20-25	-	-	
Total contamination (g/100 g)	0.02	-	-	
Sedimentation (vol %)	8.96	-	-	
Water content (% w/w)	<2	92-94	10	
Minerals	(a)	(b)	(c)	
Р	10.57	116.38	879.57	
K	5.95	173.68	1071.01	
Na	-	41.61	115.22	
Mg	-	44.52	394.85	
Ca	-	5.11	603.87	

(a) mg/kg; (b) mg/kg wet mass basis; (c) mg/g rapeseed meal.

stillage is rich in proteins and amino acids, carbon sources like soluble fibres, the rest of starch hydrolysates (dextrin), glycerol, glucose, maltose, and xylose. Main composition is depicted in Table 2.

Rapeseed meal (free flowing material resulting from rape seed pressing) is a very valuable nutritional side-stream full of proteins, digestible fibres, and minerals, mainly calcium and magnesium. The protein content is high (min. 34% in weight) (Table 2) and the stream may also contain other very interesting compounds, e.g., polyphenols which have been shown to exert positive effects on human health.

Full characterisation of the selected side-streams can be found in other EXCornsEED related publications (Lena et al., 2020a,b; Rusu et al., 2020). These facts, together with its cheapness and ready availability, support the recent studies to utilise its full potential.

2.3. Selected side-streams characterisation

A characterisation of the selected side-streams to identify the wide variety of substances known to possess effective biological

Table 3

Properties of the extractable compounds found in selected side-streams.

Extractable compound	Property	References
Bioactive peptides	Available in maize related side-streams. Several beneficial effects such as	(Díaz-Gómez et al., 2017)
	anticancer activity and properties such as antioxidant, antihypertensive,	
	hepatoprotective, and alcohol protective	
Phenolic compounds	Potential Alzheimer's disease, cancer, cardiovascular diseases, diabetes	(Ozcan et al., 2014)
Phenolic acids and	mellitus and skin disease. In particular, ferulic acid has potent antioxidant	
Flavonoids)	properties (anticancer, anti-inflammatory, anti-diabetic, hepatoprotective	
	effects, and preventive action against bone loss)	
Anthocyanins	Properties such as anti-carcinogenic, anti-atherogenic, lipid lowering,	(Rodriguez-Mateos et al., 2014)
	anti-diabetic, antimicrobial, and anti-inflammatory. It can decrease capillary	
	permeability and fragility, stimulate the immune system, and inhibit	
	platelet aggregation due to antioxidant properties	
Polyphenols	Interest in food formulations due to their ability to replace synthetic	(Del Rio et al., 2013)
	preservatives due to their free radicals scavenging activity, thus preventing	
	oxidation reactions in food	
Beta-carotene	Provitamin A activity. Strong antioxidant activity to induce apoptosis of	(Cicero and Colletti, 2017)
	cancer cells (potent chemopreventive agent in many forms of	
	gastrointestinal cancer). Furthermore, beta-carotene could enhance	
	immunity against various infectious diseases	
Xanthophylls lutein	Primary pigments for maintenance of normal visual function of the human	(Carpentier et al., 2009)
and zeaxanthin	eye macula. Strong antioxidant activity, protect humans against phototoxic	
	damage, and play a role in protection against age-related macular	
	degeneration and age-related cataract formation	
Phytosterols	Compete with cholesterol absorption in the small intestine, thus reducing	(Chawla et al., 2016)
	the supply of cholesterol in the blood stream, i.e., reduce the risk of	
	coronary heart disease and other diseases related to atherosclerosis	
Focopherols and	Strong antioxidant power and potential health effects including prevention	(Shahidi and De Camargo, 2016)
tocotrienols	of certain types of cancer, cardiovascular diseases, obesity, and diabetes.	

activities was performed in order to design an efficient extraction of individual components and valorisation of the streams. Due to their organic and bio-based nature, samples have to be analysed under different time and process conditions because of the variability of the presence and the quality of the different compounds, including potentially harmful substances such as mycotoxins, heavy metals, pesticides, and xenobiotics. Information on properties of the extractable compounds that can be found in the three selected side-streams is provided in Table 3.

3. Results and discussion. Availability and sustainability assessment.

Biofuels production dynamics are driven by the market and policy. Hence, in order to properly assess the availability of related side-streams, it is important to delve into the most relevant socio-political drivers (e.g. policies and strategies).

At the worldwide level, SDGs have become of paramount importance in relation to strategic planning and agenda shaping. Specifically, SDGs that could affect selected side-streams availability in the short-medium term are: SDG7-Affordable and Clean Energy, SDG9-Industry, Innovation and Infrastructure, and SDG12-Responsible Consumption and Production. Specifically, SDG7 could affect both positively and negatively. On the one hand, this SDG aims to increase the rate of renewable energy (Caldeira et al., 2020), which could cause countries to shape policies with incentives for the use of other renewable energy sources, decreasing the production of biofuels. On the other hand, this SDG targets the production of cleaner energy by enhancing research in this field, as well as more infrastructure investment. This could potentially cause an increase in biofuel production, increasing related sidestreams accordingly. As for SDG9, main objective is to modernise production infrastructure so they can be more sustainable and develop environmentally friendly and clean processes, which could cause bioethanol plants to update their facilities to maximise corn oil production (as has been the case for ENVIRAL) and also integrate cascading approaches for side-stream valorisation. In addition, SDG12 calls for sustainable management and use of domestic resources, which could encourage policy makers to provide guidelines on the production and use of resources (affecting corn and rapeseed meal production).

At the EU level, it is important to consider that, according to REDII, new biofuels plants need to provide min. 65% fewer direct greenhouse gas emissions (compared to the fossil fuel alternative) (European Parliament, 2018). This criterion is being implemented by EU countries, since it has been mandatory for them to transpose the directive at the latest by end of June 2021 (European Parliament, 2018). It is worth mentioning here that countries can introduce more stringent sustainability criteria. Furthermore, the Commission proposal (2021) to revise REDII promotes a gradual shift away from conventional biofuels to advanced biofuels (mainly produced from non-recyclable waste and residues) and other alternative renewable fuels (e-fuels). The EU's Biodiversity Strategy for 2030 considers that this approach should continue for all forms of bioenergy and the use of whole trees and food and feed crops for energy production should be minimised – whether produced in the EU or imported. Hence, in the medium term, policies coming from this proposal to review the REDII could affect side-streams availability.

In the USA, the most relevant policy is the Energy Independence and Security Act (EISA) of 2007, which promoted biofuel production since it requires transportation fuels sold in the USA to contain a minimum of 36 billion gallons of renewable fuels by 2022 (covering renewable fuels including corn-based ethanol, advanced biofuels, biomass-based diesel, and cellulosic biofuels).

The next subsections present the evaluated information about the selected side-streams availability. Previously in Section 1 it has already been stated that to the best knowledge of the author, no similar studies are available in the literature. However, related research in the field of bioethanol and biodiesel feedstock availability is worth mentioning, as this information is linked to the data presented herein. Jusakulvijit et al. explored the availability and evaluated potential agricultural residues for the expansion of second generation bioethanol production expansion in Thailand (Jusakulvijit et al., 2021). At the European level, a study delved into where biodiesel from rapeseed would be best produced, mapping rapeseed energy efficiency (van Duren et al., 2015). Under a similar scope, biofuel crops in Europe

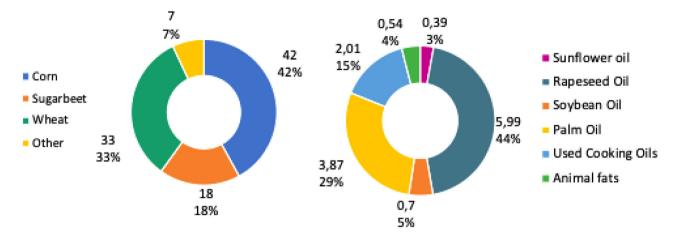


Fig. 3. (Left) Raw materials used to produce bioethanol in Europe, 2014. Own chart, data from ePure (2017); (Right) Share of rapeseed among feedstocks used in biodiesel production in the EU-28. Numbers in million tons and per cent (Kennedy, 2018). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 4

European bioethanol installed	production capacity	(ePure,	2017).	
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Country	Bioethanol installed production capacity (million litres)	Country	Bioethanol installed production capacity (million litres)
Austria	250	Italy	376
Belgium	590	Latvia	17
Bulgaria	117	Lithuania	33
Czech Republic	253	Netherlands	590
Estonia	18	Poland	869
Finland	61	Rumania	12
France	2055	Slovakia	168
Germany	1180	Spain	587
Hungary	779	Sweden	312
Ireland	10	UK	985
Total: 9262 mill	ion litres		

were explored through spatially explicit modelling (Hellmann and Verburg, 2011). Finally, about the use of other feedstocks (which is presented in Section 3.3), a feasibility analysis of biofuel feedstocks for bioethanol and biodiesel blended fuels has been performed for the Bangladesh region (Mahmud et al., 2022).

3.1. Corn oil and thin stillage availability

In recent decades, grain-to-ethanol production has increased, reaching an installed capacity of 9.262 million L in Europe (Table 4) (ePure, 2017).

Specifically, there are currently 71 bioethanol production plants in Europe (Flach et al., 2016), the main ones being in France. Germany, and Hungary, producing respectively 970 million L/year, 950 million L/year and 640 million L/year of bioethanol. It can be pointed out that in the EU, the location of biorefineries has certain correspondence with the locations of ports and chemical clusters. A large number of biorefineries are located in Belgium, the Netherlands, the Czech Republic, and industrialised areas of France, Germany and Italy (Parisi, 2018). These biorefineries use different feedstocks in their bioethanol production processes. In recent years, maize has grown in popularity as a feedstock due to its competitive price and higher ethanol yields, as highlighted in Fig. 3 (left), which shows the feedstocks used to produce ethanol in Europe (ePure, 2017). Most of the biofuel production capacity that has been built up in the EU in recent years relies on maize, while some existing plants have been refitted to process maize instead of other cereals.

Specifically, the distribution of products and side-streams obtained when processing 1 bushel of corn for bioethanol production is: 18.2 lbs of ethanol, 15.5 lbs of DDGs, 0.7 lbs of technical corn oil (Engel, 2017).

3.1.1. Corn oil

The European production of corn oil from the com bioethanol industry is expected to be approximately about 60 million L/year by 2021, counting the average of the last 3 years of ethanol production.

In terms of the USA, in 2011 only 15% of ethanol plants extracted corn oil, while in 2016 approximately 90% of ethanol plants extracted corn oil (Javasinghe, 2017). Corn oil production was 111.077 tons in 2016, today the industry recovers more than 1.5 billion kg/year of corn oil (Engel, 2017), commonly used for further biodiesel production, as it improves the biodiesel production yield. In fact, the biodiesel industry utilised approximately 39% of the total corn oil production (43.640 tons) in April 2016, reaching approximately. 51% in 2017 (US GRAINS COUNCIL, 2018). Hence, an interconnection between biodiesel production and corn oil availability can be pointed out, mostly in the USA. Furthermore, a rising trend can be identified although future estimations need to be carefully done, as these figures are usually affected by the market prices of other biodiesel feedstocks, e.g., soybean oil prices. Nowadays, it should be taken into consideration if in individual EU countries corn oil is not stated as advanced feedstock equal to national policy while interpreting the REDII. Then, the market prices of other feedstocks must be compared with the 'advantage' of 'advanced feedstock' usage.

3.1.2. Thin stillage

The average amount of thin stillage generated through bioethanol production is ca. 13 L per 1 L of bioethanol (Pejin et al., 2009), being possible to obtain up to 20 L per 1 L of ethanol. Its production in Europe, amounting to ca. 1.6 billion L/ year (110 ktons/ year), is predominantly used after further processing in solid form as DDGS for livestock feeding. Over the past years, fuel ethanol and thin stillage production rates increased with the same proportion, since thin stillage can derive from the processes of fermentation and distillation of corn or wheat, being two of the most common raw materials for bioethanol production in Canada, Europe and the U.S. (Alotaibi et al., 2014).

Finally, it is worth mentioning that thin stillage can also be derived from sugar cane or molasses, being called vinasse or distillery wastewater, although different chemical properties can be observed. Herein, thin stillage obtained from corn is considered. Other ethanol feedstocks, such as sugar cane or molasses, are discussed in Section 3.3.1.

3.2. Rapeseed meal availability

Rapeseed crops are also an emerging feedstock, as rapeseed production is more than 20 Mt/ year, making the EU the top rapeseed producer in the world. The continuous growth of rapeseed oil production is proportional to the production of press cake or meal (Lomascolo et al., 2012), which production has increased by 80% in the decade 2002-2012 (Carré and Pouzet, 2014). Specifically, worldwide rapeseed production was about 68 million tons in 2020 (Shahbandeh, 2020). In 2015, of the 9.7 million tons of rapeseed oil consumed, the proportion used for the food and biodiesel industry was 4 to 1, being the main feedstock for the biodiesel industry (60.4% in 2011, 52.3% in 2015, and 50.6% in 2016). This decline is due to the recycling of the used vegetable oil. In EU countries, rapeseed production has increased 27% since 2005 to supply the biodiesel industry. In 2015–2016, 22.3 million tons of rapeseed were produced (Gerasimchuk and Yam Koh, 2013). The European production could increase in future years, but the agricultural cost is much higher than in developing countries, so imported feedstock, such as palm oil is employed (Ismail et al., 2017). After the EU, Canada is the second, producing about 18 million tons (Carré and Pouzet, 2014).

Among the EU countries, rapeseed oil has become the main feedstock for biodiesel, as presented in Fig. 3 (right). The two largest producers in the EU are Germany and France, followed by the U.K., Poland, the Czech Republic, and Romania, which has risen its production since it takes part of the EU. Other major producers include Denmark, Sweden, Bulgaria, Austria, Hungary, and Slovakia (the two last countries also have increased the rapeseed production since their entry into EU). Furthermore, during the past 20 years, rapeseed production has increased, mainly due to Europe followed by Canada and China. Rapeseed meal is the second major oilseed meal produced worldwide (after soybean meal), with Canada and India the main exporters (Carré and Pouzet, 2014). Since the EU is deficient in protein fees, rapeseed meal consumption has grown strongly. In China, the increase in rapeseed production is due to its extraordinary economic development and in the United States to the demand for feed from milk producers.

There has been an increase in the crushing of rapeseed in the USA. Australia and Russia, joined in 2006 by the United Arab Emirates. The last 3 mentioned countries crush more than 800 kt of rapeseed/year. Worldwide, even in non-producing countries, e.g. in Mexico, it can be observed that the processing industry has been developed and the production is rising.

3.3. Other side-streams of interest as alternatives to corn and rapeseed proceeding by-products

Different types of bio-based feedstocks can be used as input for the selected side-streams valorisation process developed in the EXCornsEED project, for example, residual biomass, sidestreams of biotech industries (stillage, fugates, etc.), but also products and by-products of the food, beverages and feed industry (solid residues of oil crushing mill, DDGS from other types of biomass, pressing residues of vegetable and fruit juice, spent grains of brewers, etc.). The following sections present alternative feedstocks to corn and rapeseed-based biofuel production side-streams.

3.3.1. Starch and sugar-containing crops as alternatives to corn

Three types of raw materials containing carbohydrates have been used for ethanol production (Naik et al., 2010): (a) Sugar containing crops: Sugar cane, wheat, beet root, fruits, palm juice, etc.; (b) Starch-containing crops: Grain such as wheat, barely, rice, sweet sorghum, corn, etc. and root plants such as potatoes or cassava; and (c) Cellulosic biomass: wood and wood waste, agricultural residues, and prunings and fibres.

In Sweden, industrial ethanol generation is based on starch, mostly obtained from wheat. A starch-based facility that produces 200.000 m³ ethanol/year also produces about 2 million m³ of thin stillage and 200.000 m³ of DDGS.

Sugar beet molasses is a sugar by-product of beet processing that not only has a high carbohydrate content but is also a valuable source of many micronutrients, such as vitamins and minerals. Due to its nutritional value, molasses are used in many food and non-food processes (Krulj et al., 2014).

The second largest biomass feedstock in Europe is the barley crop waste, which has been estimated to be 25 million tons by 2030. This estimate was calculated taking into account the feedstock quantities that can be harvested without adverse impacts on the environment or existing uses treated as available for biofuel production (Lara-Serrano et al., 2018). Different studies have already highlighted the relevance of lignocellulosic biorefinery in the sustainable development of biofuels and value added products (De Bhowmick et al., 2018).

Rye (*Secale cereale* L.) is the second most common cereal in Europe since it is used for bread making. Interest in rye has recently increased due to its nutritional profile and is mainly cultivated in the Northern, Central and Eastern areas of Europe. The worldwide production is estimated to be ca.15 million tons, much lower than maize, wheat, and rice (1.000, 740, and 720 million tons, respectively). According to EU statistics, in 2016, about 8 million tons of rye were collected from 2 million ha. From 1 ton of wheat, about 0.5–2 tons of straw can be obtained (depending on the type or variety of soil), which means 4 to 16 million tons of rye straw, many of them (1.6 – 4 million tons) are used for non-agricultural purposes (Domański et al., 2017). Consequently, using rye for non-food purposes could be fragile due to its nutritional interest, even though half of its production has already been implemented for other purposes.

3.3.2. Oily seeds as alternatives to rapeseed

Oilseeds also have a place in the whole bioethanol production picture. Specifically, soybean, sunflower, mustard, and camelina are suitable for the production of meal as a source of proteins that could be used as an alternative feedstock for side-stream valorisation technologies and processes. Oilseed production is 20% of world grain production (450 million tons per year). From 1992 to 2012, the production has risen in the world, especially soybeans (2.2 times, being produced 177 Mt in 2012). By comparison, other oilseeds had a slower development: groundnuts, cottonseed and sunflower have increased 1.6 times, cereals 1.29 times and wheat 1.19 times (Carré and Pouzet, 2014). An overview of seed production is provided in Fig. 4.

Specifically, soybean meal is the main oil seed meal produced worldwide, accounting for 63% of the available meals in mass and almost 72% of the proteins supply (Carré and Pouzet, 2014).

In 2015, 20.7 million tons of oils and fats consumed (63.6%) were for food use and the remaining for the energy sector. Within this sector, 10.9 million tons were used as feedstock in the biodiesel industry, while the remainder was used in industrial applications such as energy production. The breakdown per oil seed type is provided in Table 5.

Regarding the other oilseeds, camelina (*Camelina sativa* L.) has been cultivated in Europe for over 2000 years as oil and livestock feed. The crop has recently gained increasing popularity as a biofuel source due to its oil content. Due to the presence of glucosinolates (19–23 μ mol/g) and erucic acid in camelina meal, regulations require limited daily use to avoid negative impacts on livestock productivity (Iskandarov et al., 2014). Therefore, camelina crops designated for biofuels do not compete with food

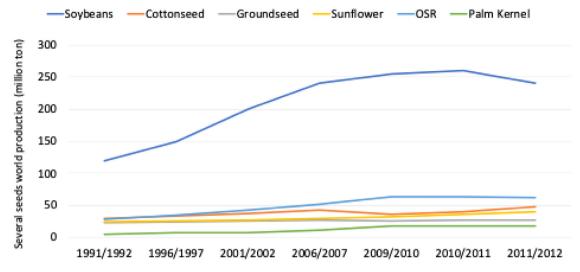


Fig. 4. World production of several seeds (Carré and Pouzet, 2014). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 5

Biodiesel production amount per corresponding feedstock in the European Union (million tons) (Ismail et al., 2017).

Item/Year	2011	2012	2013	2014	2015	2016
Production	9.34	9.74	10.65	12.20	12.37	12.35
Feedstock used:	5.51	5.7 1	10.05	12.20	12.57	12.55
Rapeseed oil	5.64	5.60	5.71	6.32	6.47	6.25
Palm oil	1.43	1.90	2.78	3.27	3.35	3.42
Used cooking oil	0.95	1.26	1.30	1.44	1.47	1.49
Soybean oil	0.84	0.42	0.29	0.49	0.48	0.58
Tallow & greases	0.33	0.36	0.41	0.43	0.44	0.44
Sunflower seed oil	0.11	0.13	0.08	0.17	0.10	N/a
Others	0.05	0.05	0.10	0.09	N/a	N/a
Others	0.05	0.05	0.10	0.09	N/a	

crops. To meet future demand, new camelina-based cropping systems are needed. On the other hand, some estimates indicate that the northern US state of Montana alone could support between 0.8 and 1.2 million ha of camelina per year. Camelina growth yields anywhere from 336 to 2240 kg of seeds per ha at maturity, with the lipid content of individual seeds ranging from 35 to 45 weight percent (% w/w). Therefore, the resulting yield of camelina oil is calculated to be between 106 and 907 L/ ha, which is higher than soybean and sunflower oils but less than rapeseed oil (965–1342 L/ha for rapeseed, 347–562 L/ha for soybean and 505–750 L/ha for sunflower) (Moser, 2010).

The production cost of mustard oil is lower than that of rapeseed or canola, although it is relatively a new feedstock for biodiesel production. Mustard plant can be grown in dry areas and requires less pesticides and other agricultural inputs than rapeseed. Excessive amount of erucic acid (more than 50%) generally makes it non-edible and is therefore mostly used as condiment and pickles. According to the Pakistan Economic Survey (2013-2014), the mustard crop was grown over an area of 220.000 ha with an annual production of 203.000 tons. The annual production of mustard oil in Pakistan is higher than its consumption. It makes mustard oil a suitable option for use as a source of biodiesel (Shahzadi et al., 2018). According to the Food and Agriculture Organization of the United Nations (FAOSTAT), the world mustard production in 2009 was 661.326 tons, and Canada was the main producer with 208.300 tons, USA 22.391 tons together accounting for 230.691 tons in North America. The mustard production on the European continent was 215.492 tons (Ukraine 118.200 tons, Russian Federation 23.690 tons). In Asia, mustard production was 213.628 tons (Nepal 135.494 tons, China 18.000 tons).

4. Conclusions

Biorefineries are gaining relevance as sustainable alternatives to fossil-based energy. Since there is a wide variety of biorefinery side-streams that could be valorised to their full extent, the current and future production rates assessment is relevant in order to prioritise valorisation approaches as well as to back-up investment decisions.

A case study for feedstock including rapeseed meal, corn oil, and thin stillage from biofuels production and alternative effluents with replication potential is presented. In summary, there is a growing trend towards the use of renewable resources that is directly related to biofuels production. The determining factors are: market price developments, regional availability of fossil fuels, geopolitical strategies and dynamics (e.g. those triggered by SDG commitments), regulatory measures to promote energy expansion from renewable sources, and increased society awareness of issues such as sustainability and climate protection. However, it is important to pay attention to market prices in the different regions, as these have proven to be a particularly important driver in the use of different sources for biofuels production (affecting therefore the availability of co-products and side-streams). This becomes of paramount importance for the availability of corn oil, as its use for biodiesel production is linked to oily seeds and biofuel prices. Also, it is worth mentioning the link between thin stillage and corn oil and how market prices could affect their availability since both have the same source.

Therefore, it can be drafted that the trend in biofuel markets (supported by regional policies) leads to increased production of biofuels, which also determines an increased availability of the selected side-streams. Regarding corn oil, an average production in Europe of 60 million L/year can be quantified. Additionally, 1.6

billion L/year of thin stillage are produced. Concerning rapeseed meal, 68 million tons/year are produced worldwide.

The main limitations of the current study are related to difficulties experienced when looking for information due to the inherent problem of officially quantifying by-products, co-products, and side-streams due to formal denominations as waste or residue and End-of-life state consideration according to the different approaches that European and national regulations pose (e.g., the Waste Framework Directive (European Parliament, 2018)).

Finally, in terms of future research to be done, the results presented in this paper can be considered as the first step for the development of innovative high-valued valorisation processes using biofuel production side-streams as feedstock. In this context, it would be desirable to extend the study to side-streams from other biofuel production processes, i.e. second and third generation biofuels. Similarly, since the data presented in this article focus mainly on Europe and the US, it would be very useful to expand the study to the South American and Asian regions. After the analysis that has been performed, it is also considered that an assessment of the production potential of bioactive compounds would be very interesting, considering the number and capacity of existing biorefineries and the composition of the selected sidestreams. In the opinion of the authors, this "map" of type and availability of valuable substances of interest would stimulate the development of sustainable valorisation technologies.

CRediT authorship contribution statement

Marta Macias Aragonés: Conceptualisation, Methodology, Validation, Investigation, Resources, Writing – original draft, Writing – review & editing, Visualisation, Supervision. Carmen Girón Domínguez: Methodology, Investigation, Resources, Writing – original draft, Writing – review & editing, Visualisation. Petra Ondrejíčková: Conceptualisation, Validation, Investigation, Resources, Writing – review & editing, Supervision. Fátima Arroyo Torralvo: Resources, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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