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Developing an integrated supercritical fluid biorefinery for the processing of grains

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ABSTRACT

With the rapid growth of the bioeconomy, there are major developments in the biorefinery concept to maximize utilization of renewable resources, including grains of cereals and oilseeds, targeting applications not only in food, nutraceutical, pharmaceutical and cosmetic products but also in biofuel, biochemical and biomaterial sectors. Supercritical carbon dioxide (SC-CO_2) technology could have a major role to play in modern biorefineries. Know-how has been building on individual unit operations based on SC-CO_2, especially extraction, fractionation and reactions involving lipids and particle formation for delivery of bioactives as summarized in this study mostly based on the previous work of the authors. Based on a solid understanding of fundamentals, the focus is now on optimal integration of these unit operations to build supercritical biorefineries. Such approaches should also consider integration of supercritical operations with conventional technologies for efficient and optimal process design. Even though the future of supercritical biorefineries seems to be bright, offering numerous advantages, there are also some substantial technical and economic challenges requiring further research.

1. Introduction

Over the past 25 years, significant progress has been made toward better understanding of the fundamentals and exploring new opportunities offered by supercritical fluids for processing of natural materials thanks to the efforts of researchers around the world. Based on these efforts, supercritical carbon dioxide (SC-CO_2) has been proven to be an excellent alternative to organic solvents for the extraction of lipids, which has led to the installation of commercial plants for the recovery of oils. Some examples of such commercial supercritical operations, focusing on lipid-based oils obtained from plant materials are listed in Table 1, where the use of SC-CO_2 as the extraction solvent is promoted by the companies. Majority of the products listed in Table 1 are specialty oils, which are low-volume and high-value products due their high content of polyunsaturated fatty acids and bioactives like phytosterols, carotenoids, tocopherols, tocotrienols and others. Expanding the utilization of SC-CO_2 technology to the processing of high-volume commodity raw materials such as grains of cereals and oilseeds requires us to take full advantage of the benefits of SC-CO_2 by taking a more integrated approach to process development and not just be limited to extraction alone. Latest developments in biorefinery approaches create new opportunities for SC-CO_2 processing.

Limited supply of petroleum resources together with the ever increasing demand for petroleum-based products has fueled the emergence of the bioeconomy. Global trends highlight the growth in fuel, energy, materials, chemicals and other products based on renewable feedstocks as economically viable alternatives to petroleum-based products. This has led to the biorefinery concept, which is analogous to a petroleum refinery, where renewable feedstocks, instead of nonrenewable fossil fuels, are converted into chemicals, fuel, materials and other products. Thus, a biorefinery would integrate a variety of separation and conversion processes to produce multiple product streams from renewable feedstocks with little or no waste. Industrial-scale integrated biorefineries are critical for the growth of a sustainable bioeconomy.

Such developments in biorefinery approaches force us to consider integrated approaches to utilization of supercritical technology in biorefining. In addition to some of the conventional separation and conversion technologies, supercritical fluid technology could play a major role in developing an integrated biorefinery, considering the well-known advantages of SC-CO_2. Instead of considering supercritical fluid extraction (SFE) as an isolated single step process, it should be evaluated as the starting point to obtain

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Table 1
Examples of commercial specialty oil products, rich in polyunsaturated fatty acids, phytosterols, carotenoids and/or tocopherols extracted using SC-CO_2 from various plant sources[1].

Company	Location	Raw material for lipid-based oil extracts	Reference (web sites accessed on Sept. 17, 2014)
Aromtech	Findland	Seeds of blackcurrant and lingonberry Seabuckthorn berries	www.aromtech.com
Flavex	Germany	Seeds of borage, chia, evening primrose, fenugreek, kiwi, millet, pomegranate and raspberry; berries of saw palmetto and seabuckthorn; hazelnut; soy germ; wheat bran	www.flavex.com
NateCO_2	Germany	Saw palmetto and seabuckthorn berries	www.nateco2.de
Flaveko Trade spol. s.r.o.	Czech Republic	Seeds of evening primrose, borage, amaranth; saw palmetto berries	www.supercriticalextraction.eu
Feyecon	The Netherlands	Plant oils	www.feyecon.com
Proderna Biotech	India–The Netherlands	Seeds of flax, pomegranate and amaranth; seabuckthorn berries	www.proderna.com
UMax	South Korea	Sesame seed	Ref. [1]
Honsea Sunshine Biotech	China	Seeds of evening primrose and pomegranate; seabuckthorn berries	www.honseabio.com
Valensa Inernational	USA	Seeds of perilla and chia; saw palmetto berries	www.valensa.com
MOR Supercritical LLC	USA	Corn germ	www.reyntek.com/MOR/SC

[1] *Source:* Personal communication, Dr. Jerry W. King, Professor Emeritus, University of Arkansas.

lipids from grains that can be used as is or as the feed material for conversion to other higher value products such as nutraceuticals, biomaterials and biofuels. If an investment is to be made to solubilize lipids in high pressure CO_2, then the return on that investment should be maximized by exploring all possibilities of separations and conversions under supercritical conditions at an incremental additional cost prior to depressurization and recovery of the extracted components. Over the years, the know-how has been building on other unit operations, including fractionation, reactions and particle formation. However, an integrated supercritical biorefinery development is at its very early stages because current supercritical processing of lipid-rich grains focuses mainly on extraction, fractionation and conversion as single unit operations, being far from a fully integrated system, despite the fact that supercritical fluid technology offers a great deal of flexibility in this regard. Therefore, the next phase in the supercritical process development and design for grains should focus on the optimal integration of unit operations onto an extraction step and understanding the fundamentals required for such integration to develop a feasible SC-CO_2 biorefinery. In addition, integration of supercritical operations with other conventional unit operations of separations and conversions should not be overlooked in an effort to explore novel opportunities for SC-CO_2-based operations within existing processes.

In her previous review article, providing some perspectives on the processing of fats and oils using SC-CO_2, Temelli [2] suggested a scheme for the potential use of supercritical fluid processing in an integrated biorefinery. In keeping with the goals of the Workshop on Supercritical Fluids and Energy (SFE'13) held in Campinas, Brazil, December 8-11, 2013, the objectives of the current article are to review the recent activities on the various biorefining approaches for lipid-rich grains using SC-CO_2, to identify what is missing in our state of knowledge and to highlight some perspectives on what needs to be done for developing an integrated SC-CO_2 biorefinery for the processing of grains.

2. Feedstock for biorefineries

Grains of cereals and oilseeds are ideal sources of renewable feedstock for biorefineries. Similar to any other biological material, grains are composed of lipids, proteins, carbohydrates, moisture, ash and other minor components. Most of the conventional processes result in underutilization of the grains by focusing on only one or a limited number of components of the grains; therefore, the full value of grains is underestimated. The use of SC-CO_2 would target the extraction of lipids, while the remaining proteins and carbohydrates can be further fractionated using conventional processes. Thus, the use of petroleum-based organic solvents can be avoided, especially for the lipid fractions and their product applications in food, nutraceutical, pharmaceutical and cosmetic industries can be targeted with no concern for solvent residues. In addition, some fractions and conversion products can target utilization in biofuel, biochemical, biomaterial and other industrial sectors. This would lead to a balanced approach for maximum utilization of grains, avoiding the 'food vs fuel' competition for our valuable agricultural commodities.

Another potential grain-based feedstock for a SC-CO_2-based biorefinery is dried distillers' grains with solubles (DDGS), which is a by-product of the bio-ethanol industry. The increasing demand for ethanol as a fuel substitute has resulted in a dramatic increase in the number of ethanol plants in North America. Corn is the major grain source used for bio-ethanol production in USA, whereas it is wheat in Canada, Australia and in some European countries. With such tremendous growth of the bio-ethanol industry, vast amounts of DDGS and CO_2 are produced as by-products. DDGS is the dried residue, remaining after the starch fraction is fermented to produce ethanol. The thin stillage left after ethanol fermentation contains solubilized components and is added back to solids prior to drying to obtain DDGS. Currently, DDGS is mainly utilized as livestock feed; however, it is a more valuable material that can yield high-value fractions. Major components of corn DDGS are 33.7% protein, 11.2% lipid and 43.6% carbohydrates [3]. Its composition, low cost and availability in vast amounts make DDGS an excellent feedstock for further biorefining. Integration of SC-CO_2 operations with bio-ethanol production can be a win–win situation creating new uses for CO_2 generated as a result of fermentation. DGGS comes in dry and ground form, which is ready for SC-CO_2 extraction and no further treatment is needed prior to SC-CO_2 processing. As well, starch in the original grain is removed, leaving lipids more concentrated in the DDGS residue. Therefore, it is worthwhile to consider if SC-CO_2-based operations can be added onto existing bio-ethanol facilities and whether it is necessary to dry the DDGS completely before it is fed to a SC-CO_2 extractor.

3. Supercritical biorefinery concept for grains

In an integrated biorefinery, the first major stage would focus on the separation processes to fractionate the major and minor components of grain feedstock. Then, in the second