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Review

The extraction and fractionation of specialty lipids using near critical fluids

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ABSTRACT

The state-of-the-art and progress achieved in the extraction and fractionation of selected specialty lipids using near critical fluids is briefly reviewed, and opinions are provided on what is still to be achieved, and future directions for further research and development. The selected specialty lipids are high value seed oils, polyunsaturated fatty acid concentrates, carotenoids, and phospholipids. High value seed oils are produced commercially using supercritical fluids, and supercritical CO_2 extraction technology is well established. The opportunities for further development include the use of new gases, and the inclusion of in situ refining into the extraction process. The extraction and fractionation of polyunsaturated fatty acids to produce concentrates has had limited commercial success, despite the extensive research that has been carried out in this area. The future direction for research and development could focus on the combination of enzymes and supercritical fluids for fractionation of lipids; and the extraction of lipids from the industrial fermentation of micro-organisms in which the polyunsaturated fatty acids are already concentrated. The extraction of astaxanthin from microalgae has been commercialized. Further work is warranted in the extraction of carotenoids from micro-organisms, especially using propane or dimethylether as the solvent. The extraction and fractionation of phospholipids is an area that has technical challenges, but shows considerable promise for the development of new lipid products. CO_2 can only extract neutral lipids from lipid mixtures, and a co-solvent such as ethanol must also be used to extract phospholipids. In contrast, propane and dimethylether can be used without co-solvents to extract both polar lipids and also carotenoids. The future challenges in the extraction and fractionation of specialty lipids are to achieve integration of supercritical extraction with other processing and refining operations, and to use new extraction solvents where feasible.

Contents

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1. Introduction

Lipids are one of the three main macronutrients, and are essential to many functions in the human body, as well as being a source of energy. Lipids are usually categorized as being neutral or polar. The term neutral lipid (NL) is taken to be those lipids that do not contain charged or highly polar groups. This includes triglycerides and partial glycerides, carotenoids, sterols, fatty acids, fatty acid esters and a limited range of hydrocarbons that naturally appear in some fish and seed oils, such as squalene. Neutral lipids are largely used for energy production, with excess being stored in the body as fatty deposits. Complex lipids are those lipids that contain at least a fatty acid or equivalent hydrocarbon chain and at least one highly polar or charged group. Typical classes of complex lipids include phospholipids (PL), glycolipids, ceramides, cerebrosides and gangliosides. They are usually found in the body in cell membranes and have specialized bioactive roles within the body. Here, we have taken specialty lipids to be lipid extracts or ingredients that are low volume and of sufficiently high value that they warrant production using supercritical technologies. This high value is usually as a result of at least one of the following factors, including health benefits of the lipids, propensity to degradation during processing (e.g. polyunsaturated fatty acids), small market size, and/or difficulty in isolation or concentration using conventional processing technologies. The specialty lipids that are reviewed in this paper include high value seed oils, neutral lipids containing polyunsaturated fatty acids, carotenoids, and specialty phospholipids. Minor neutral lipid components (squalene, tocopherols and plant sterols) also fit into the category of specialty lipids, but are not reviewed here.

2. High value seed oils

High value seed oils are taken to be those that contain one or more polyunsaturated fatty acids with desirable bioactivity. The most commonly extracted oils are those that are rich in gamma-linolenic acid (GLA or C18:3 ω-6) and/or alpha-linolenic acid (ALA or C18:3 ω-3). The extraction of these high value specialty seed oils has reached a commercial stage. The most commonly investigated seeds are Evening Primrose, Borage, Blackcurrant, Kiwifruit seed, Hemp seed, and Rosehip seed [1]. Table 1 lists the important fatty acids in these oils, and the total lipid yield by supercritical extraction.

The key to extraction of the seed oil at an industrial scale is to ensure that the seeds are well ground, to expose as much of the available oil to the solvent [3], but not so finely ground that the seeds agglomerate and/or overheat, which can cause the oil to degrade. The seeds should be ground just prior to extraction, to minimize oxidation. In general, no one grinder will suit every type of seed. The choice of grinder depends on the seed hardness, seed size and oil content. For example, blackcurrant seed is small and very hard and so a pinmill can be used, whilst borage seed is relatively soft and the oil is easily extruded, and so a roller mill or screw press can be used. If the seeds are optimally ground, the rate of extraction of the oil is dominated by the solubility of the oil in supercritical CO_2. The solubility is a function of the temperature, pressure, and average molecular mass of the oil [4,5]. Typical extraction curves for a variety of oils processed at a laboratory and pilot scale are shown in Fig. 1 at constant extraction conditions of 300 bar and 313 K. The relationship between molecular mass and solubility at 300 bar and 313 K derived from Fig. 1 and from the literature is shown in Fig. 2 [6,7]. The extraction curves all have a constant extraction rate period, followed by a falling rate period in which the oil loading drops off. Typically, the oil extracted during this period becomes darker, due to the extraction of less soluble

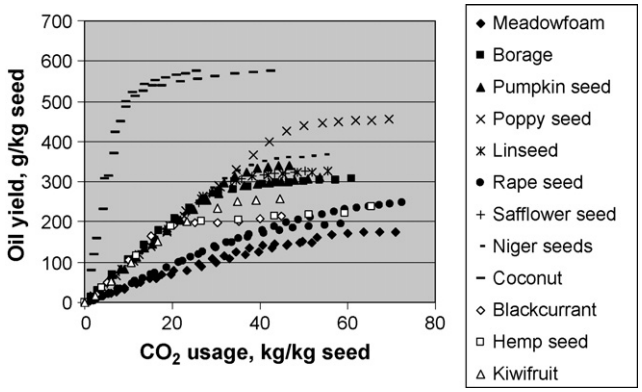

Fig. 1. Extraction curves for 12 seeds oils at a laboratory scale using supercritical CO_2 at 300 bar and 313 K [2].

pigments and natural antioxidants. CO_2 is no longer saturated with oil, as the effective bed length is now shorter than that required to achieve saturation. Water is usually co-extracted with the oil, and can mostly be removed from the oil by fractionating the extract into two fractions through the use of two separators. Water, essential oil (if any) and undesirable free fatty acids are largely collected in the second separator. Oils extracted using supercritical CO_2 tend to have low levels of antioxidants, and can have high free fatty acid and peroxide levels [8,9].

The throughput of seed and production of oil in a supercritical CO_2 extraction plant tends to be limited both by the solubility of the oil in supercritical CO_2 and the high content of oil in the seeds. This limitation is shown clearly by the long constant rate section of the extraction curves for most seeds as shown in Fig. 1. The extraction rate is then limited by the CO_2 circulation rate through the plant, which in turn is limited by the pressure drop over the bed of seeds. This limitation results in poor utilization of the available extraction vessels in a typical extraction plant, as the solvent becomes saturated over a short length of extraction bed, and thus only one extraction vessel is effectively extracted at a time if the beds are extracted in series. Extraction at a very high pressure (>500 bar) increases the rate at which oil can be extracted due to an increase in solubility of the oil [5,6], but leads to co-extraction of undesirable pigments, and high pressure drops over an extraction vessel because of the increase in viscosity. Another approach for a multi-vessel plant with high CO_2 flow capacity is to extract the beds of seeds in parallel flow, and to have the vessels staggered in terms of the degree of extraction. Thus, at any time for a three-vessel plant,

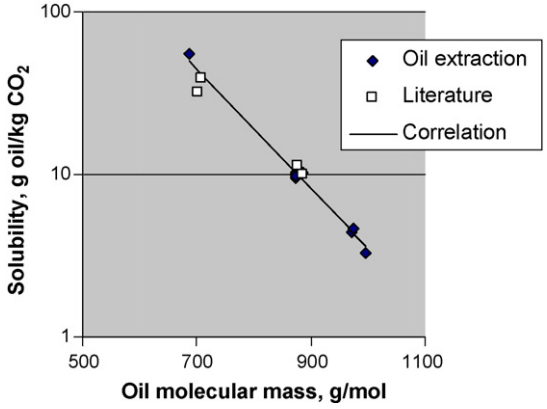

Fig. 2. Solubility of seed oils in supercritical CO_2 at 300 bar and 313 K as a function of oil molecular mass, solid symbols are from oil extraction data shown in Fig. 1, hollow symbols are literature data [6,7].