Rapeseed proteins for the chemical industry: Extraction, isolation and modification

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Introduction

Rapeseed press cake and meal are produced in vast amounts as residual materials during oil extraction. Due to their high content of valuable proteins, these materials are currently used as animal feed or purified to produce protein isolates for the food sector.[1] However, the utilization is limited due to remaining antinutritive components, such as phytates and glucosinolates. A promising alternative to overcome these hurdles is the utilization of rapeseed proteins in the chemical industry. With their great functionality, such as foaming, emulsifying and film-forming properties, rapeseed proteins offer a renewable alternative to petro-based ingredients in products such as coatings, detergents or polymers.

Methods

Rapeseed press cakes were defatted with isohexane in a percolator and flash desolventized with superheated isohexane at 400–500 mbar prior to steam desolventizing at a maximum product temperature of 60 °C. Protein extraction was carried out in aqueous solution (c_{NaCl} = 0.25 M) at various pH values. Enzyme-assisted processes were carried out at pH 9 using 1% Protease A-01 ($w/w_{Protein}$). Protein isolation was performed by ultrafiltration or combined acidic precipitation and ultrafiltration. Rapeseed protein concentrates were further modified by enzymatic hydrolysis or chemical modification using lauroyl, stearoyl or oleoyl chloride. Chemical composition and functionalities (protein solubility, foaming, emulsifying and film-forming properties) were analysed for all rapeseed protein concentrates.

Results

Protein solubility was analyzed for five different rapeseed raw materials ranging from industrially toasted meal to lab-scale non-pressed meal (Figure 1).[2] The negative impact of industrial rapeseed processing was highlighted by strongly reduced protein solubility of residual materials. Cold pressed meal and pre-pressed meal were selected for a detailed study of protein extraction and isolation conditions. Cold-pressed meal showed significantly higher protein extractability under all tested conditions (solid to liquid ratio, extraction time, temperature, pH value, concentration of sodium chloride). However, for protease-assisted processes, protein extraction yields of both raw materials were similarly high (Figure 1). Thus, utilization of proteases is a valuable method to increase protein extractability from intensively processed materials.

Protein isolation was carried out by two processes: i) ultrafiltration or ii) acidic precipitation followed by ultrafiltration.[3] Protein yields obtained from these isolation procedures were mainly dependant on the initial extraction yield. Protein preparations showed protein contents of 75.3%–88.0% (based on dry matter content and a nitrogen-to-protein conversion factor of 5.7) and were thus categorized as protein concentrates. The three types of protein concentrates obtained through these processes showed distinct solubility profiles and functional properties (Figure 2). High solubility was achieved for ultrafiltrated samples, especially when low-soluble proteins were removed by a previous precipitation step. Additionally, ultrafiltrated protein concentrates showed great foaming and emulsifying properties, making them particularly valuable for products such as foamed adhesives or emulsion-based lubricants. In contrast, precipitated protein concentrates showed low solubility and lower values for foaming and emulsifying properties than the ultrafiltrated samples, presumably due to a high level of irreversible protein denaturation upon precipitation.
Additionally, modification of functional properties was carried out by enzymatic hydrolysis using Protease A-01 (Figure 2). The method proved to be a valuable tool to enhance protein solubility of low-soluble preparations up to >90% in the full pH range. Foaming properties were also strongly improved, while emulsifying capacity was decreased compared to the precipitated concentrate.

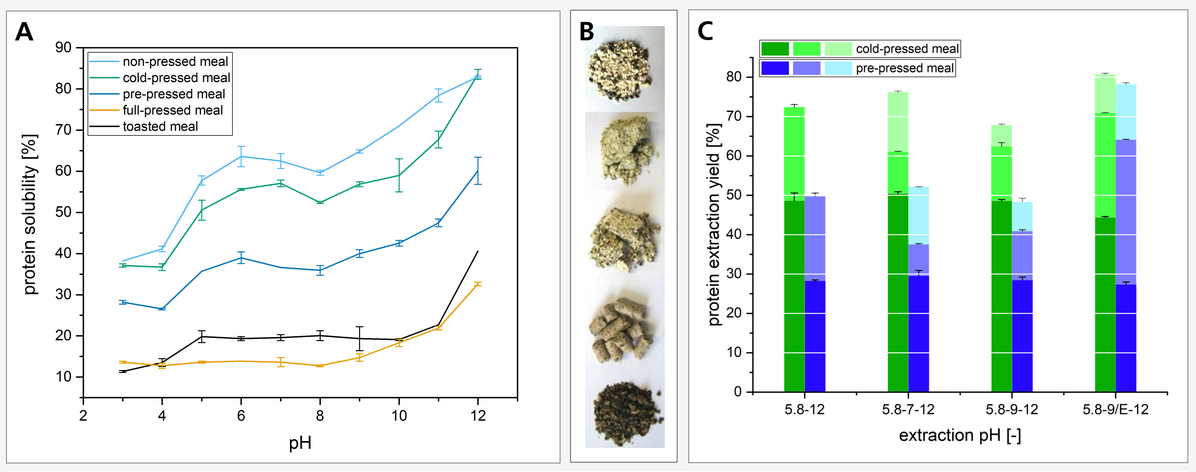
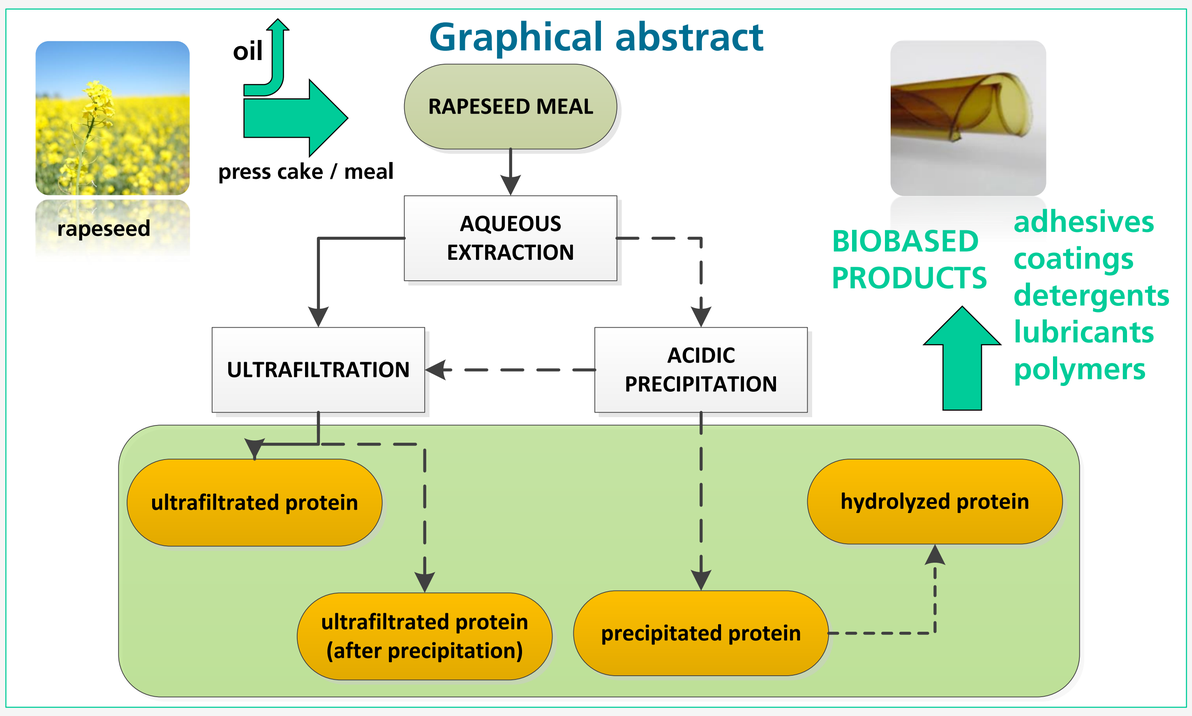
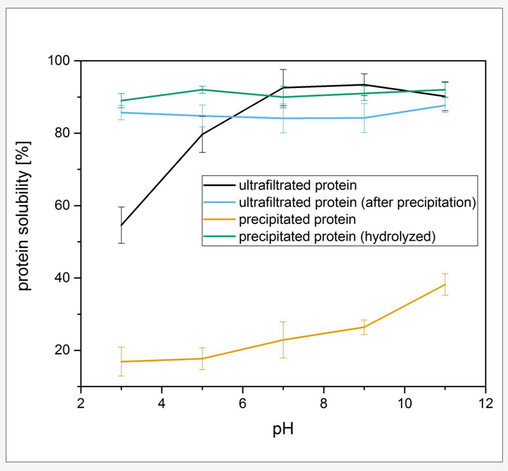


Figure 1. (adapted from [2])
A. Protein solubilities of rapeseed raw materials.
B. Photographs of rapeseed raw materials (from top to bottom: non-pressed meal, cold-pressed meal, pre-pressed meal, full pressed meal, toasted meal.
C. Protein extraction yields obtained from multi-step extractions at different pH (5.8, 7, 9, 12) and with an enzyme dosage of 1% Protease A-01 for a three-step process (pH 5.8-9/E-12).

The negative impact of industrial rapeseed processing is highlighted by reduced protein solubility of residual materials, resulting in lower protein extractions yields. This can be overcome by the use of proteases during the extraction process.

Graphical abstract





type	foaming activity [%]	foam stability [%]	foam density [g/L]	emulsifying capacity [mL/g]
ultrafiltrated	1834–2834	92–97	33–52	688–735
ultrafiltrated (after precip.)	2040–2876	92–99	33–47	666-756
precipitated	842–1043	86–93	94–175	413–445
hydrolyzed	3132–3316	90–94	27–29	330–340

Figure 2. Protein solubility (left) and functional properties (above) of rapeseed protein concentrates.[3]

Rapeseed protein concentrates show distinct functional properties depending on isolation strategy and modification.

Results (continued)

Film-forming properties of rapeseed proteins were demonstrated in previous studies.[4,5] All protein concentrates obtained in the present study showed good film-forming properties in cast-film experiments using glycerol as a plasticizer. Film-forming properties are of high relevance to a number of technical applications, such as adhesives, coatings, detergents, lubricants and polymers. As low water-stability of protein films can be a limiting factor in these applications, chemical modification of rapeseed proteins was carried out to increase their hydrophobic properties. Rapeseed protein concentrates were modified using fatty acid chlorides by the Schotten-Baumann-reaction. Subsequently, cast-films were analyzed regarding their mechanical and barrier properties. While the films were still water-soluble, an increase of surface hydrophobicity which correlated with the degree of modification could be determined.[6]

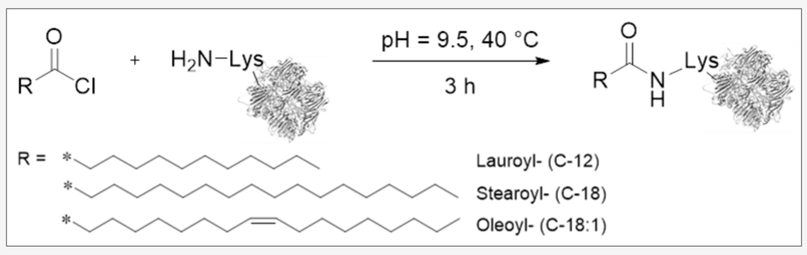


Figure 3. General reaction scheme for the chemical modification of rapeseed proteins using fatty acid chlorides (Schotten-Baumann-reaction).

Surface hydrophobicity of rapeseed protein films is increased by chemical modification.

Conclusion

Rapeseed proteins offer a promising alternative to petro-based ingredients in the chemical industry. For an economic production, care has to be taken when choosing the defatting process in order to limit negative impacts on protein extractability. Different functionalities can be achieved depending on isolation strategy and subsequent modification steps. Currently, a number of possible application fields for rapeseed proteins are being investigated within the project "TeFuProt" (tefuprot.de).

Acknowledgements

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