



Simultaneous production of lignin and polysaccharide rich aqueous solutions by microwave-assisted hydrothermal treatment of rapeseed meal



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ABSTRACT

This work addresses a novel and green process for the co-production of lignin and oligosaccharides from rapeseed meal, examining the effects of the temperature (150–210 °C), reaction time (0–60 min) and catalyst amount (1–4 mol/L, CH₃COOH) on the process. The yields to gas, liquid and solid varied by 0–18%, 22–64% and 34–74%, respectively. The solid consisted of high purity lignin (26–88 wt.%) together with unreacted cellulose (0–28 wt.%), hemicellulose (0–28 wt.%) and proteins (11–28 wt.%). Increasing the temperature and/or reaction time produced an increase in the liquid yield and a decrease in the solid yield due to the solubilisation of the cellulosic and hemicellulosic contents of the feedstock. Acetic acid exerted a positive catalytic effect, promoting the solubilisation of cellulose and hemicellulose and preventing humins formation. The relative amounts (wt.%) of C, H, O and N in the solid fraction shifted between 46–63, 5.8–6.4, 28–42 and 2–6, respectively. Py-GC/MS analysis revealed that the solid decomposed into phenols (1–19%), sugars (0–15%), N-compounds (0–31%), carboxylic acids (37–75%), hydrocarbons (4–20%) and furans (1–8%). The liquid phase comprised oligo- and mono/di-saccharides (33–51 C-wt.%, 0–3 C-wt.% and 0–6 C-wt.%) and carboxylic acids (40–62 C-wt.%). The progressive solubilisation of cellulose and hemicellulose produced an increase in the proportion of C together with a decrease in the amounts of H and O in the solid product, which also accounted for the increase and decrease observed in the proportions of phenols and sugars, respectively. An optimum was found at 186 °C using an acid concentration of 1 mol/L and a total reaction time of 2 min. These conditions maximise the solubilisation of cellulose and hemicellulose without altering the lignin content of the solid; thus allowing the selective and simultaneous production of high purity (85 wt.%) lignin together with a rich oligosaccharide (51 C-wt.%) solution. The acid can be recovered from the sugar mixture, which not only improves the efficiency of the process but also allows the production of a pure saccharide (92 C-wt.%) product.

1. Introduction

Rapeseed, the third largest source of vegetable oil in the world, is currently used for the production of both edible oil and biodiesel [1]. During the processing of rapeseed seeds to produce the oil, around 65 wt.% of the feedstock is converted into a lignocellulosic solid residue called rapeseed meal or rapeseed cake [2,3]. This solid material is mainly composed of cellulose, hemicellulose, lignin and proteins; the precise chemical composition of the residue depending on the type of rapeseed plant and extraction process [2]. Traditionally, rapeseed meal has been used as a livestock feed due to the presence of proteins in the residue. However, the increase in biodiesel production has oversaturated the agricultural market and new processes and alternative strategies need to be developed for the valorisation of this feedstock [4].

In this context, two alternative options have normally been

considered for the valorisation of rapeseed meal. The first is the application of different extraction systems to recover valuable products. In this respect, Purkayastha et al. [5] analysed the effectiveness of several solvents for the extraction of residual oils and polyphenols from a rapeseed cake at 25 °C for 2 h. It was found that non-polar solvents were the most effective in recovering the residual oil. Terpin et al. [6] investigated the extraction of polyphenols from *Camelina* linseed, rapeseed and white mustard using methanol and ethanol at room temperature for 12 h. They found that the plant material and the extraction solvent not only significantly influenced the amount of phenols extracted, but also the antioxidant properties of the extracts. Li et al. [7] investigated the use of pressurised solvent systems to recover phenols, analysing the effects of the solvent type (ethanol, methanol, 2-propanol, acetone and acetonitrile) and concentration, temperature (80–200 °C) and time (2–30 min). The use of a 60 vol.% methanol/water solution at 200 °C for 20 min extracted the highest amount of phenols (93 mg/g).

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The second option relies on the use of thermochemical processes, such as pyrolysis, gasification, combustion and hydrothermal treatments to produce bio-fuels, energy and value-added chemicals. Özçimen et al. [8] examined the production of bio-oil and bio-char from a rapeseed cake produced during oil extraction from *Brassica Napus*. The pyrolysis experiments were performed in a fixed bed reactor at 500 °C, employing different gas space velocities (50–300 cm³/min). Regardless of the space velocity, around 73% of the rapeseed meal was converted into bio-oil (60%), bio-char (27%) and permanent gases (13%). The valorisation of this type of cake was also investigated by Ucar et al. [9] who analysed the effect of the reaction temperature (400–900 °C) during the pyrolysis of the residue. The gas consisted of CO₂, CO, CH₄ and H₂S, while the bio-oil was made up of carboxylic acids, amides and phenols. An increase in the temperature increased and decreased the gas (8–14%) and char (30–38%) yields, respectively; while the bio-oil yield increased between 400 and 500 °C (14–19%) and slightly decreased with further increasing the temperature up to 900 °C. Giannakopoulou et al. [1] conducted catalytic pressurised pyrolysis experiments of a spent rapeseed meal produced during the production of biodiesel. Two catalysts (H-ZSM-5 and H-Beta zeolites) and two reactor configurations (a pressurised pyrolysis unit, and a pressurised pyrolysis unit with catalytic upgrading of the pyrolysis vapours) were tested. In the process, two liquid phases (aqueous and organic), gases and a solid residue were obtained. The organic phase was made up of aliphatic and aromatic hydrocarbons, carboxylic acids, esters, nitriles, amides, poly-phenols and N-heterocyclic compounds. The liquid phase consisted of a mixture of phenols, ketones, alcohols and heterocyclic and N-heterocyclic compounds.

Pinkowska et al. [3] studied the hydrothermolysis of rapeseed meal using sub-critical water for the recovery of fatty acids and amino acids, examining the effects of the reaction time and temperature on the process. The maximum yield of amino acids (136 g/kg of rapeseed cake) took place when the solid was treated at 215 °C for 26 min. A further increase in the temperature led to the decomposition of the amino acids. The maximum fatty acid production (0.91 g/kg) occurred at 246 °C using a reaction time of 65 min. Briones et al. [4] explored the possibility of co-valorising two biodiesel by-products: crude glycerol and rapeseed meal. The effects of the mass/solvent ratio, temperature and reaction time on rapeseed meal valorisation were experimentally investigated. In the process, the cellulose, hemicellulose and lignin contents of the solid were decomposed, leading to the production of a liquid mixture consisting of glycols, carboxylic acids, furans esters and ethers. Egües et al. [2] employed a two-step process for the production of saccharides from rapeseed meal pellets. Firstly, the hemicellulose content of the feed was extracted and purified; then, this fraction was converted into saccharides by auto-hydrolysis or acid hydrolysis. Glucose and xylose were the main sugars identified in the hydrolysates; their specific amounts depending on the hydrolysis process. In the case of auto-hydrolysis, they accounted for 23% and 40%, respectively, while their relative amounts were 28% and 37%, when acid hydrolysis was used.

Another interesting option for the valorisation of rapeseed meal that has not been considered before is the simultaneous production of saccharides and pure lignin from the solid aiming to build a bio-refinery concept around this residue. However, the extraction of polysaccharide-free lignin from biomass is very challenging because lignin is strongly covalent bonded to cellulose and hemicellulose, which hinders the selective extraction of pure lignin. Therefore, the development of a suitable method for lignin isolation is of paramount importance for the production of pure lignin from biomass. In this respect, the two-step Klason acidolysis method is one of the most widespread used [10]. However, its major drawback is the use of concentrated sulphuric acid, which is not environmentally friendly and also damages the lignin structure. Another method is the combination of biomass milling, to break the linkages between lignin and saccharides, followed by solvent extraction using a dioxane-water solvent system [11]. Though, this

latter methodology is considered extremely time-consuming as a reaction time as long as 3 weeks is needed in some cases. This led to the modification of this latter methodology using enzymes to increase the lignin yield; nevertheless, the lignin yield was still low and a high enzyme dosage was needed [10].

Therefore, more research needs to be conducted for the development of novel and energy efficient methodologies for lignin production from biomass. As part of this, the use of microwave heating has recently appeared as a new and promising alternative. Microwave heating is based on the high frequency rotation of polar molecules, which produces a quicker and higher heating of the species with higher polarity within the biomass structure [12]. As lignin has a higher aromaticity, i.e. lower polarity, than cellulose and hemicellulose, it is less active during microwave heating [13]. This could allow the separation of cellulose and hemicellulose from the biomass without significantly altering the lignin structure; thus allowing a high purity lignin to be produced. In addition, as water is highly effective in microwave energy absorption, the combination of hydrothermal conditions together with microwave-assisted heating might be an interesting new technology for the valorisation of rapeseed meal. To the best of the authors' knowledge, the work conducted using microwave assisted hydrothermal conditions for the extraction of lignin from biomass is very scarce. In particular, Zhou et al. [14] used formic acid to extract lignin from birch biomass employing conventional and microwave heating. A higher amount of delignification was reported when microwave heating was used in the experiments. Li et al. [15] studied the effect of the temperature (90–109 °C) during the isolation of lignin from bamboo. The temperature was found to significantly influence the process and the use of higher temperatures resulted in a greater lignin yield. Zoia et al. [16] conducted microwave assisted lignin isolation using HCl and reported that their methodology was capable of recovering up to 55 wt.% of the total lignin present in the material. Zhou et al. [13,17] addressed the effects of the temperature (160–210 °C) and reaction time (5–20 min) during the isolation of lignin from softwood employing H₂SO₄. They found that an increase in both the temperature and reaction time increased the lignin yield and purity. Maxima for the yield (82 wt.%) and purity (93 wt.%) occurred using a 0.2 mol/L sulphuric acid solution at 190 °C for 10 min. The liquid phase consisted of a mixture of saccharides, carboxylic acids and furans and was found to have potential to be used in fermentation processes.

Given this background, this work addresses the valorisation of rapeseed meal by means of a microwave-assisted hydrothermal process catalysed by acetic acid, a much safer and greener alternative to mineral acids, for the simultaneous production of pure lignin and polysaccharide rich aqueous solutions. In particular, the effects of the temperature (150–210 °C), time (0–1 h) and catalyst (acetic acid) amount (1–4 mol/L) together with all the possible interactions between these variables on rapeseed meal valorisation have been thoroughly analysed. Given that the microwave-assisted hydrothermal valorisation of rapeseed meal has never been reported before and the works dealing with the isolation of lignin from biomass using microwave technology are very scarce, this work represents a novel and challenging investigation not only for the management and valorisation of rapeseed meal, but also for the development of a novel, quick and environmentally-friendly methodology for the production of pure lignin and saccharides from other types of biomass. In addition, the fact that acetic acid can be directly produced from biomass and the use of an energy efficient microwave-assisted hydrothermal process convert this process into a green, efficient and sustainable route for biomass valorisation.

2. Experimental

2.1. Microwave experiments

A CEM Discover II microwave facility was used for the experiments.

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