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# MAXIMUM RECOVERY OF DIFFERENT TYPES OF BERRY BYPRODUCTS
# MAKSIMALNO KORIŠĆENJE RAZLIČITIH NUZ PROIZVODA IZ BOBIČASTOG VOĆA

*Dr. Cecilia, HODÚR, Sándor BESZÉDES, Szabolcs, KERTÉSZ, Angéla, SZÉP, Dr. Zsuzsanna, LÁSZLÓ, Dr. Gábor SZABÓ,*
*University of Szeged, Institute of Mechanical and Process Engineering,*
*e-mail: hodur@mk.u-szeged.hu*

## *SUMMARY*

*The main element of juice technologies is squeezing. The juices are very rich in useful components such as vitamins, colorants, sugars, minerals, amino acids, etc, but the extraction from the tissues is never complete, as numerous valuable components remain in the press-cakes. Classical methods of using these components include fermentation and/or compost preparation. The aim of this work was to extract some of the valuable components, e.g. pectin or galacturonic acid, from the press-cake of red currant (Ribes rubrum) and to achieve a better biodegradability of the residuum of the cake for enhancing biogas product. In the case of examination of pectin extraction the classical hot-water process and the microwave assisted extraction at 5 -25 W/g specific microwave power level were compared. The experiments show that microwave assisted extraction, compared to hot water extraction, reduced the processing time from 6-8 h to 30 min, the pectin yield was higher and, the liquid phase demand could be lowered. The residual carbohydrates of the cake can be used for biogas production. The rate of conversion into biogas is much higher after MW treatment than for the untreated samples, and there is a similar tendency in the biodegradability of MW-treated samples.*

***Key words**: berry byproducts; microwave assisted extraction, pectin, biodegradability, biogas*

## INTRODUCTION

The food and agricultural industries are producing increasing amounts of liquid and solid wastes. In the case of fruit process a large amount of marc is produced as residual of squeezing. The enzymatic pectin hydrolysis is suitable to enhance the yield of squeezed juice, but the mass of press cake is less decreased. Because of high water content the marc is less resistant to enzymatic and microbial destruction hereby many kinds of valuable and utilizable component go to waste. The common utilization of marc is alcoholic fermentation, animal feeding or composting. But during these processes, the bioactive components, antioxidants and vitamins vanish.

The berries of red currant contain pectin and antioxidants and a large amount of these components was retained in the marc. The extraction of utilizable component (pectin, antioxidants) can be beneficial from economical and environmental aspects. The byproduct of extraction process is suitable to anaerobic digestion or 2$^{nd}$ generation bioethanol producing through the high cellulose content.

Natural pectin is a structural unit of fresh cell and a junction between the cells advanced land plants. It exists between the cell walls and its function is to agglutinate the cells to form a compact junction. The pectin consists of a-D-galacturonic acid components, which are partially esterified with methyl alcohol at carboxylic acid end. Pectin has been used in the food industry as a thickener, texturizer, emulsifier and stabilizer, and as a gelling agent in jams and jellies. It has also been utilized as a filler or stabilizer in confections, dairy products, fruit preparations, bakery fillings, icings and frostings. Other applications include fat replacers in spreads, salad dressings, ice cream and emulsified meat products.

The most used raw materials of commercial pectin extraction processes are apple, orange, sugar beet, berries (e.g. blackcurrant). In the case of the last one, the by-product of blackcurrant juice pressing contains a great deal of valuable components such as pectin, which are worthwhile to recover. The commercial pectin extraction processes are based on degradation by acid and deposition. These processes are very time consuming, taking from 1 to 12 h, and have a large liquid phase demand. In these processes an acidic solution is used, by applying sulphuric, phosphoric, nitric, acetic or hydrochloric acid, and a temperature range from 80 to 100 °C. These conditions may also result in protein and polysaccharide degradation and, therefore, they can negatively affect both the quantity and the quality of extracted pectin. Because of the time and reactant demands of this process, it appears necessary to develop a new procedure, by which the pectin could be extracted in a shorter time in better quality. These reasons have led to the application of improved, rapid extraction processes, such as microwave assisted extraction (MAE).

Microwave heating is used as a popular alternative to conventional heating mainly due to considerable reaction time reducing and so-called non-thermal microwave effects. In recent years, MAE attracted a growing interest, as it allows rapid extractions of solutes from solid matrices, with extraction efficiency comparable to that of classical techniques. In this type of extraction, microwave energy is used to heat solvents in contact with samples to extract valuable and soluble compounds from the sample into the extractant, such as pectin from apple pomace [1], lime and orange peels [2]. Microwave irradiation causes disruption of the interactions which bind biopolymers together by dipole rotation or orientation effects. The MW orientation effect is mainly a result of polarized parts of macromolecules lining up with the poles of the electromagnetic field which can lead to the breaking of hydrogen bonds [3]. Orientation (athermic) and subsequent heating (thermic) effects are presumed to break the polymeric network, releasing mainly extracellular and possibly intracellular materials such as polysaccharides and proteins into the soluble phase. The efficiency of microwave energy is dependent on the dielectric properties of solvent and the sample.

As strongly polar solvent, water can efficiently absorb the microwave energy and transform it into thermal energy, leading to rapid heating of the sample. During microwave treatments the cells were thermally stressed, continuously raising the temperature of the cells and the cell walls are ruptured. Thus the skin tissues are opened up by the microwaves more rapidly and extensively than in the conventional hot water method [4].

Besides the acceleration of pectin extraction, the microwave irradiation can enhance the biodegradability of lignocelluloses residuals. Because of thermal and athermal effect the microwave treatments enhance the rate of the biodegradability of biopoly-

mers. Although MW treatment has also been reported as a rapid method for cell lysis, its application as a pretreatment process in anaerobic digestion of sewage sludge is mentioned only. These effects may be demonstrated by a difference in the ratio of the chemical oxygen demand (COD) and the biochemical oxygen demand (BOD), and by an increased rate of biogas production from various biopolymer wastes. After pectin extraction process, marc consists of a polymeric network formed by extracellular polymeric substances and cells that are resistant to direct aerobic and anaerobic degradation, since cell walls and extracellular polymeric substances present significant physical and chemical barriers [5]. The microwave irradiation at appropriate specific power level is suitable for rapid degradation of extracellular polymeric substances and increases the efficiency of hydrolysis of macromolecules which is the most limiting step of anaerobic decomposition and biogas production processes.

In his paper the efficiency of classical hot-water extraction and the microwave assisted extraction process (MAE) were examined. In the case of by-products of pectin extraction the enhancing of the efficiency of biogas production by microwave treatment was also examined.

## MATERIALS AND METHODS

For our experiments red currant (*Ribes rubrum*) press-cake was used. The press-cakes originated from a Hungarian berry farm (Fitomark 94 Ltd), where the raw material was treated with pectinase to increase the yield of juice before the squeezing process. After pressing, the marc was frozen at –22 °C. The moisture content of the marc (on a wet basis) was 74.7% The moisture content was determined by drying 10 g of sample at 105 °C for 24 h in a drying cabinet.

For the conventional extraction, an Armfield (Hampshire, Great Britain) pilot solvent extractor was used. The solvent was water at 80 °C, with pH 6.18 without any adjustment, and water adjusted with aqueous hydrochloric acid solution to pH 2. The quantity of sample was 100 g, the solid-liquid ratio was 1:40 and the applied volumetric flow rate of solvent was 0.33 L/min.

For microwave assisted extraction (MAE) a single-mode cavity resonator was used, at 2.45 GHz magnetron frequency. The microwave power of the magnetron is continuously adjustable between 100 and 700 W. The treatments were carried out in a covered PTFE sample holder to prevent evaporation during the irradiation without pressure increase. Temperatures were measured with an infrared thermometer. The specific microwave power level was changeable by varying the power of the magnetron using constant sample quantities (28 g). The specific power levels applied were 5, 10, 15 and 25 W/g wet weight, and the experiments were carried out during 10 to 40 minutes. The solid-liquid ratio varied between 1:5-1:20.

The extracted pectin content was measured photometrically at 520 nm by the m-hydroxydiphenyl method adapted from Ibarz et al. [6], and expressed in GA units. A standard curve absorbance/concentration was fitted with the absorbance values at 525 nm from different series of D-galacturonic acid concentration solution. All analyses were performed in triplicate.

The biodegradability (BD) was characterized by the $BOD_5$/COD ratio. The chemical oxygen demand (COD) was measured according to the dichromate standard method in COD test tubes with an ET 108 digester and a Lovibond PC Checkit COD photometer. The biochemical oxygen demand (BOD) measurements were carried out in a respirometric BOD meter (BOD Oxidirect, Lovibond, Germany), at 20 °C for 5 days. To ensure the consistency of the results BOD microbe capsules (Cole Parmer, USA) were used for measurements. Biodegradability during 5 days ($BD_5$%) was characterized by the following expression:

$$BD_5\% = \frac{BOD_5}{COD} \times 100\%$$

By biogas measurements the cumulative biogas digestion tests were performed in batch mode under mesophilic conditions, at 40°C for 30 day, in a temperature controlled anaerobic digester with Oxitop Control type pressure mode measuring system (WTW Gmbh., Germany). The digesters were inoculated with an acclimated anaerobic sludge from an operating biogas reactor of municipal wastewater treatment plant (Hódmezővásárhely, Hungary) in order to eliminate the possible lag-phase of biological degradation process. After inoculation nitrogen gas was flowed through the reactor to prevent exposure to air.

The measurements were performed in two bottles: in one of them, the total biogas content was measured, while in the other, the methane content was determined by absorbing the $CO_2$ content produced in KOH solution. The resulting pressure difference is proportional to the $CO_2$ concentration; the remaining overpressure is proportional to the $CH_4$ content.

## RESULTS AND DISCUSSION

Firstly, commercial hot water and acidic hot water extraction was investigated for the extraction of pectin residues, and the pectin content of the extracts was determined. The results of the extracted water-soluble pectin content for 8 hours' duration of extraction are depicted in Fig. 1.

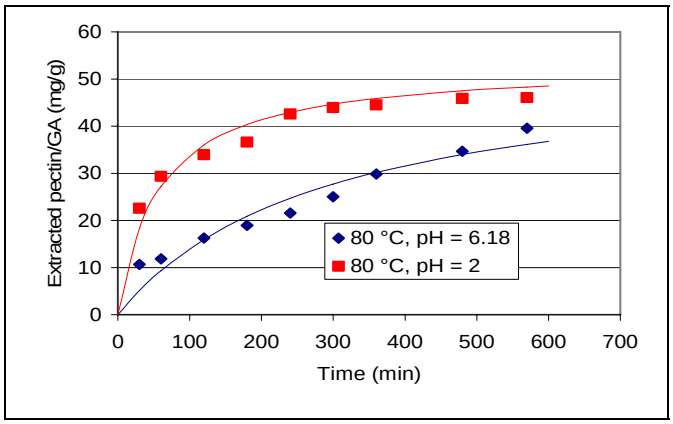


*Fig. 1. Effect of pH on pectin yield by classical hot-water extraction*

*Sl.1. Efekat pH na prinos pektina pomoću klasične ekstrakcije vrelom vodom*

The results showed that the pH has a considerably effect on pectin yield in the case of classical hot water pectin extraction process. The connection of initial pectin yield and extraction time is approximately linear, but at acidic pH (pH=2) the rate of pectin extraction is higher than at non pH-adjusted solvent. At acidic pH saturation value was observed after 400 minutes extraction but in the case of near neutral pH saturation value of curve was not achieved in the examined extraction time period. The higher extraction rate can be explained in that at lower pH the cell lysis of the marc is more expressed, so that more pectin can be released from the hemicelluloses matrix. In summary, the pH is a hardly determinative process parameter by classical hot-water extraction but the decreasing of pH under 1.5-2.0 units is not legitimated because of large scale hydrolysis of extracted pectin.

In the next series of our measurements, the pectin yield from red currant press cake was investigated by applying microwave

assisted extraction process. The applied specific microwave power was between 5 - 25 W/g, at pH = 6.18, with a solid-liquid ratio of 1:10. The effects of microwave power level, solid to liquid ratio and the pH of solution were investigated. The yield of pectin increased as the specific MW power was increased. The relationship between pectin yield and time differed, depending on the specific MW power applied. At lower power levels (5 -10 W/g) the correlation between the duration of extraction and the pectin yield was linear.

At higher levels (15-25 W/g) there was logarithmic relationship between these parameters indicating saturation. The higher specific MW power level produced an intensification effect, generally from the beginning of extraction. The benefit of the application of higher specific microwave power level was an intensification effect in the beginning of extraction (Fig. 2).

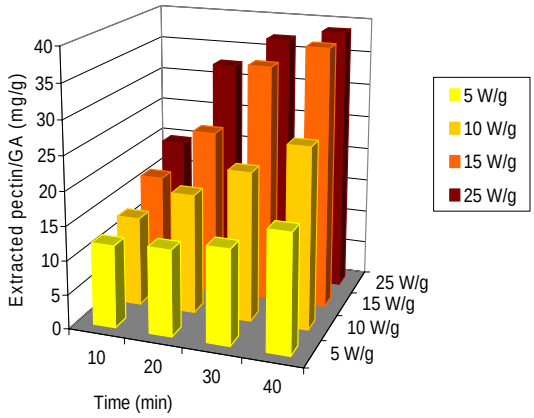


*Fig. 2. Effect of specific power level and treatment time by MAE*
*Sl. 2. Uticaj specifičnog nivoa snage na vreme tretana pomoću MAE*

After extraction the residuals are rich in polysaccharides mainly lignocelluloses. The biological degradability of celluloses is poor through the compact and complex structure of macromolecules. The microwave irradiation can modify the structure of celluloses. So, on one hand the pectin is released into the water phase during the MAE, on the other hand the biodegradability of residuals increased. The effect of microwave irradiation was characterized by the change of 5 days biodegradability ($BD_5$%), given by the ratio of $BOD_5$/COD.

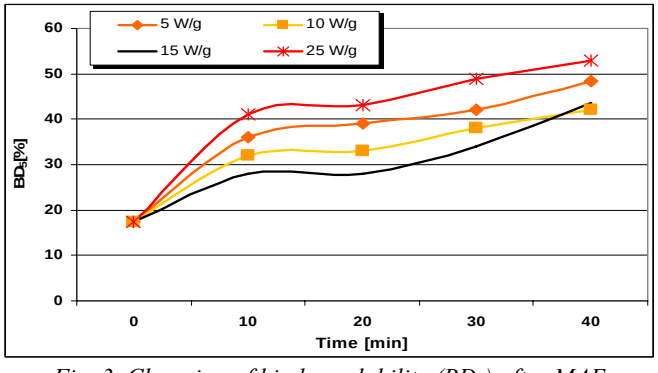


*Fig. 3. Changing of biodegradability ($BD_5$) after MAE*
*Sl. 3. Promene biorazgradljivosti ($BD_5$) posle MAE*

The increasing of irradiation time definitely enhances biodegradability. The enhancing of specific microwave power level from 5 W/g to 10 or 15 W/g caused decreasing of biodegradability, which can be explained in that less easily biodegradable compounds (pectin, simple carbohydrates) are released from the marc and the relative amount of less degradable component is increased. At higher microwave power level this decreasing effect was compensated by the enhanced thermally hydrolysis of macromolecules via higher irradiated microwave energy. So in the case of 25 W/g microwave treatment a higher biodegradability was experienced (Fig. 3).

By biogas product of microwave irradiated marc the advantageous effect of higher specific power level was showed up better.

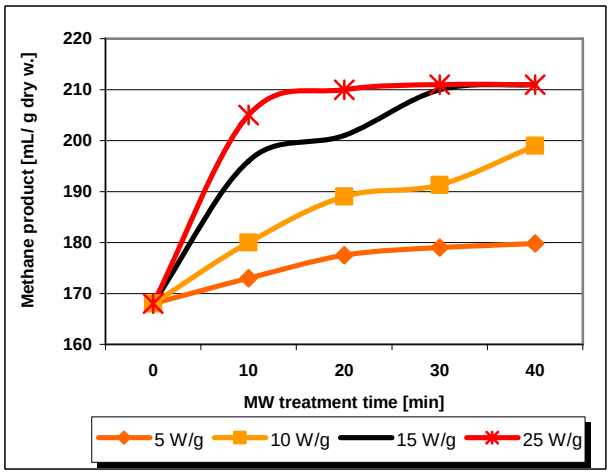


*Fig. 4. The biogas product of marc after MAE*
*Sl. 4. Proizvodnja biogasa posle MAE*

At higher microwave power level (15 and 25 W/g) saturation value was observed in the cumulative biogas product and there was no significant difference between the methane yield of 15 and 25 W/g extracted samples after 30 minutes microwave irradiation (Fig. 4).

## CONCLUSION

The experiments show that, as compared to hot water extraction, microwave assisted extraction reduced the processing time from 6-8 h to 30 min, the pectin yield was higher and, the liquid phase demand could be lowered. The biogas product increased by enhanced microwave power level and enhanced treatment time. To summarize, the microwave treatment accelerated the pectin extraction and enhanced the amount of produced biogas, so it is suitable for applying in full recovery by-products processes of berries.

## LITERATURE


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