Supercritical Fluid Extraction Using Microwave Heating

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To compare conventional heating and microwave irradiation for supercritical extraction process a new SFE apparatus was built. Model experiments were carried out using CO_2 at moderate temperatures and pressures up to 20 MPa to study the influence of dielectric heating in combination with supercritical extraction. The results of extract were determined quantitatively by weighting the product and qualitatively by chromatography. The microwave heating (MSFE) shows advantages like short heating time, loss energy consuming and sharp temperature profiles can be applied to MSFE. Results will be shown and discussed.

INTRODUCTION

Over the past few years supercritical fluid extraction has acquired increased significance. Supercritical fluids especially carbon dioxide, ethane or propane with or without modifier have found a lot of applications mainly in the field of natural product extraction for foodstuff, cosmetic and pharmaceutic industry 81, 2].

Supercritical fluid extraction is a technique which takes advantage of the enhanced solvent power of supercritical fluids. The advantage of supercritical fluids lies in the change of properties like density or viscosity. They are in between those of gas and liquid. After the expansion of the fluid the residue extract are without impurities by solvents. Supercritical fluid extraction has been demonstrated to be a valuable alternative for oil or fat extraction, because a relatively rapid process can be carried out under mild conditions and at low temperatures.

Up to now, microwave assisted extraction is only used in combination with inorganic or organic solvents (e.g. water, ethanol, chloroform). Recently, microwave-assisted extraction has received increasing attention by greatly reducing the extraction time with similar and even higher efficiency then the conventional Soxhlet extraction [3].

The aim of this work is to compare in a SFE process conventional heating with microwave heating. A combination of supercritical extraction and microwave heating seems promising to connect the advantages of both methods.

EXPERIMENT

The new MSFE apparatus is mainly a combination of a high pressure equipment (XO1-500-AF (120 °C-Y)) of SITEC, Zurich, Switzerland, and a modified microwave autoclave (MLS-µltraClave II) of the MLS GmbH, Leutkirch, Germany. The equipment is shown schematically in figure 1. The microwave transparent extraction cell (glass cylinder closed on

the lower site by a frit, used volume 5 l, weight of sample ca. 300 g) is placed on the cap of the high pressure autoclave. The fluid stream flows through the glass frit from down to the top of the sample. The microwave energy can be adjusted between 0 and 1 kW. Therefore a flexible continuous volume heating is possible and temperature gradients in the sample can be avoid.
The double-walled autoclave allowed alternatively an external heating of the autoclave without microwave irradiation by use of a thermostat. Therefore the same apparatus can be used for extractions under classical and non-classical conditions lead to comparable results.

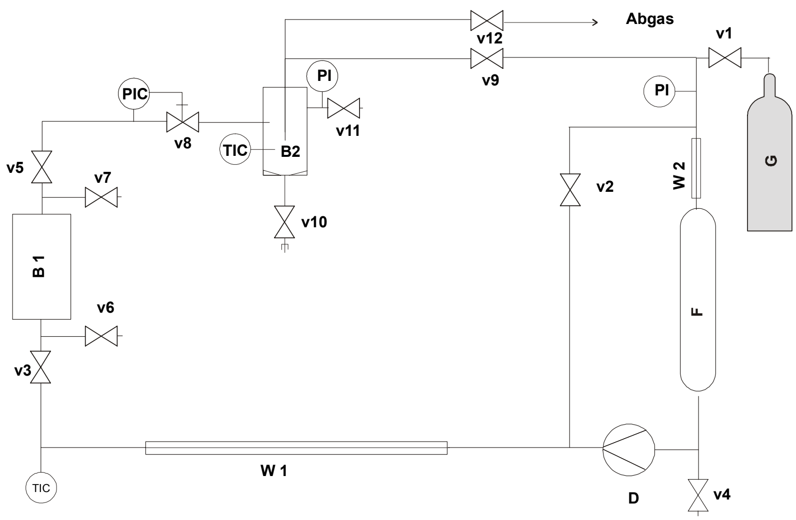

Figure 1: B1 MW-Extractor, B2 Separator, D Dosing pump, F Fluidstorage, G Gas, W1 heat exchanger, W2 Fluidcondenser, v1 – v12 volves, PI + PIC pressure gauge, TIC Temperature gauge.

The required pressure was achieved by a compressor using commercial available carbon dioxide from a gas cylinder. For the extraction experiments an average flow rate of 6.5 l/min carbon dioxide were used, controlled by a manual needle valve. The separation of soluble compounds from the supercritical fluid is carried out by total expansion in a separator.
The used microwave frequency (24.125 GHz) is adjust to water properties and therefore microwaves are absorbed by water molecules excellent. Samples used in this work (in MSFE or SFE) are moisten by water to improve the microwave absorption and heating. The influence of water content to microwave heating in MSFE or SFE processes will be discussed in an additional paper.

RESULTS AND DISCUSSION

As expected, the use of microwave heating shows some technological advantages. At first the heat-up time was reduced drastic.
Figure 2 shows different temperatures during the starting procedure and heat up to prepare an SFE process as function of time. By conventional heating more then a half hour was needed

to reach the working temperature (Vessel temperature). The set temperature was 60 °C, the thermostat temperature started at 75 °C and was adjusted step by step to reach the set temperature "very soon". The actual extraction temperature in the sample (here Oenothera biennis) was reached after 90 minutes. The intake of the fluid (here CO_2, p = 12 MPa) increased the temperature gradient and shortened the heat up time. Because of the sluggish temperature regulation by the external thermostat an exact temperature controlling is almost difficult.

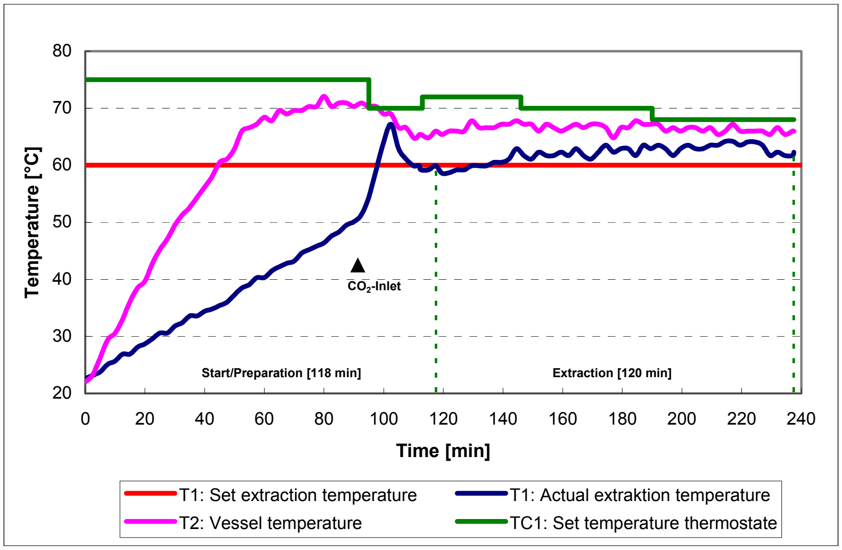

Figure 2: Temperatures during starting procedure and heat up in classical SFE-process as function of time, Sample: Oenothera biennis, p = 12 MPa, Fluid: CO_2.

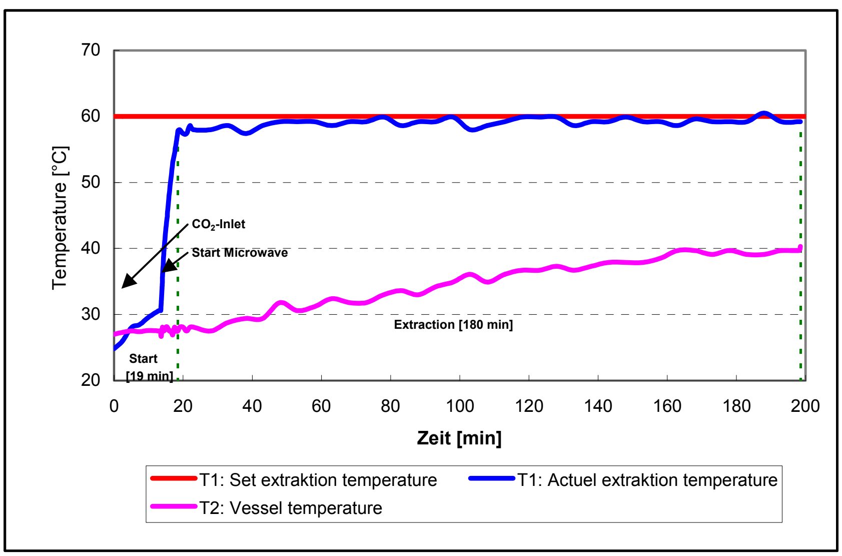

Figure 3: Temperatures during starting procedure and heat up in microwave assisted SFE-process as function of time, Sample: Oenothera biennis, p = 12 MPa, Fluid: CO_2.

In figure 3 the same circumstances as in figure 2 are shown if microwave heating is used for SFE process. Less than 20 minutes were needed to reach the extraction temperature in the sample. After increasing the pressure to extraction pressure a very steep temperature increase can be observed and only a time of 3 – 5 minutes is necessary to start the MSFE process. Also an exact temperature controlling is possible because of the flexibility of microwave heating. The vessel temperature increase slowly with time and reached ca. 40 °C at the end of the MSFE process.

Every variation in the flow rate resulted in temperature variation of the extraction probe. In contrast by gently microwave irradiation the extraction temperature was adjusted already after about two minutes, independent from the speed of the fluid stream.

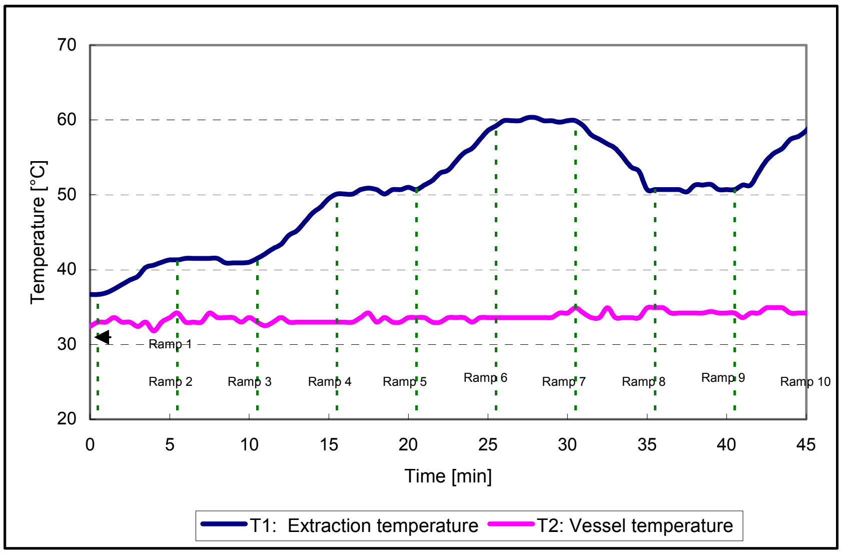

Figure 4: Measured temperature course in sample by applying a temperature program on MSFE process as function of time, sample: Oenothera biennis, p = 12 MPa, Fluid: CO_2.

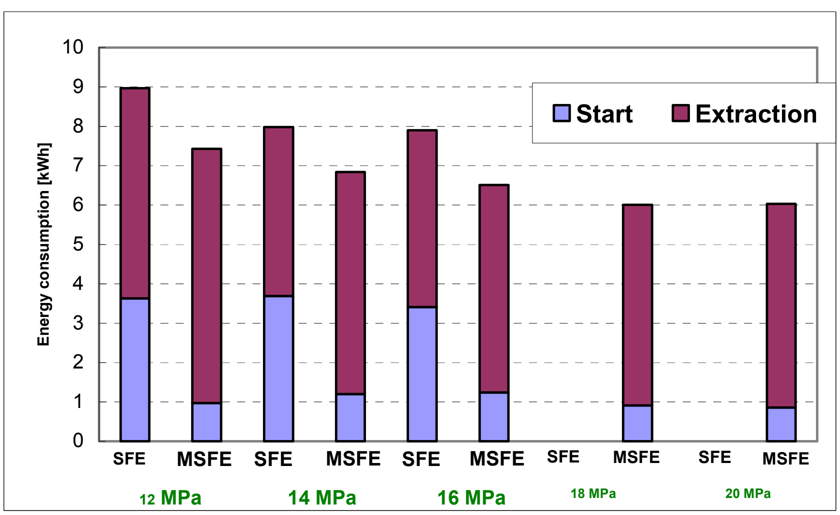

Figure 5: Energy consumption: SFE – MSFE for different pressure, sample: Oenothera biennis, T = 60°C, fluid: CO_2

In figure 4 the measured temperature course by applying a temperature program on MSFE process as function of time is shown. Different temperature steps were used to test the flexibility of microwave heating in SFE process. First a temperature step of 10 °C per 5 minutes was applied and than the temperature was hold constant during next 5 minutes. The measured actual temperature in sample (here Oenothera biennis, T = 60°C, Fluid: CO_2) follows exactly the applied temperature. This makes it possible to apply temperature programs to MSFE processes. Maybe this leads to a selective extraction (and separation) controlled by temperature. Also the thermal (and mechanical) stress of the sample and the extract can be reduced to a minimum of time.
Because of the short heat up time in case of MSFE energy can be saved. Figure 5 compares the energy consumption of a SFE and a MSFE process for different pressure (sample: Oenothera biennis, T = 60°C, fluid: CO_2). As expected the MSFE process needs 20 % of energy less than the conventional SFE process. The difference comes from the starting procedure because of the heating of the complete autoclave to reach the extraction temperature. In case of MSFE only the sample is heated.

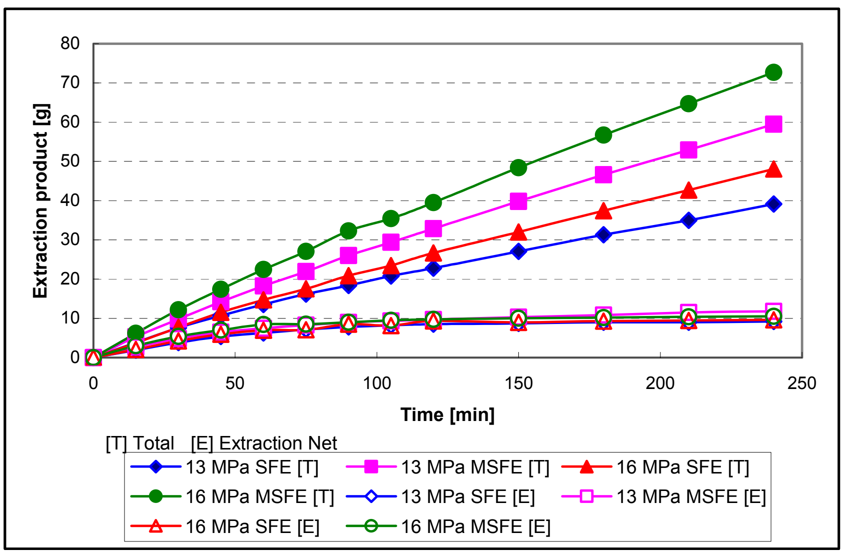

Figure 6: Extraction product of caraway seeds as function of extraction time for different pressures, SFE conventional SFE, MSFE Microwave assisted SFE

Results of the different extraction methods of caraway seeds are shown in figure 6. The extraction experiments were carried out at pressures of 13 and 16 MPa. In all cases the use of microwave irradiation leaded to higher amounts total extract which includes water and etheric oil. After separation of oil and water the amount of extract is exactly the same and did not depend on the extraction process.
Differences in general composition of the extract were not observed. In relating of the main compounds the products were total identical. Apart from one or two traces at the same pressure the chromatograms are identical in number and high of peaks at the same.

CONCLUSION

Compare to the conventional heating in SFE processes the MSFE shows several advantages:

- avoid temperature gradients by volume heating
- short heat up time (max. 3 - 5 min.) and short cool down time
- simple and flexible process control of temperature
- allows temperature programs independent of equipment and fluid flow
- only sample is heated
- less energy and time needed
- minimizing of thermal stress of sample
- Constant temperature during SFE, independent of flow rate

GC-analysis of the product pointed out that microwaves have no influence on selectivity of extraction. Finally the microwave heating allowed a handling by only modest heat up of reactor materials. Therefore a frequently exchange of extraction samples is possible without long cool down time.

OUTLOOK

To come to a final assessment of MSFE compare to SFE the following additional questions have to be answered:

- Is selective extraction possible using temperature programs ?
- What is the influence of water content to MSFE ?
- Is there optimum water content for MSFE ?

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