Solvent-free, integrated Process for by-products from fats and lipid manufacturing

Eun-Hee Lee, Sang-Kyu Shin[1], Byung-Soo Chun[1], Andreas Weber[*]
GoshenBiotech
[1]Pukyong National University
(weber@igoshen.com[*])

Introduction

Manufacturing lipid products from natural resources normally yields significant amounts of low-value fats and oils next to the focused high valued processes. With better refining technologies these rests can be turned into valuable products or at least converted into useful energy sources. Fats are possible to be converted by alcoholysis into fatty acid esters which can be used instead of petroleum in ovens or diesel engines to provide thermal or electrical energy. As an alternative to the chemical hydrolysis, which can be difficult to control, the biochemical conversion by lipase is uncomplicated to carry out [1, 2]. This process generates fatty acid monoglycerides next to fatty acid esters. Monoglycerides are widely used as emulsifiers in the food industry and yield higher market prices than oils. The energetic use of fatty acid esters can improve the energy balance of the enzymatic process.

Enzymatic reactions which are carried out in supercritical carbon dioxide can take advantage of higher mass transfer rates than under classical conditions [3]. Next to that supercritical carbon dioxide can be used to extract products continuously from the substrate. Because of the significant differences of the thermodynamic properties of the generated products the pressure and temperature of the supercritical fluid can be chosen in a way that only the generated fatty acid esters are withdrawn from the reaction mixture. It is also possible to extract monoglycerides and separate them from the fatty acid esters by a two-stage depressurization in two subsequently arranged separation vessels

Experimental works

Materials

Household grade corn oil (Ottogi corn oil, Korea) was used in transesterification reactions with ethanol (technical grade, 95%, Korean Ethanol Supplies Company). Different kinds of immobilized lipase were used including Novozyme 435, Lipozyme TL-IM, and Lipozyme-RM (Novozymes A/S, Bagsvaerd, Denmark). Methanol, isopropanol and hexane used in the analytics were HPLC grade (J.T. Baker).

Transesterification Experiments

A laboratory scale supercritical fluid plant depicted in Figure 1 was build-up for the purpose of enzymatic reaction- and the selective extraction of product components. The plant consists of a reactor with a magnetically driven blade stirrer (550 ml, 40 MPa, 100 °C), and three separators (150 ml, 15 MPa, 100 °C). Carbon dioxide is fed by a Lewa LDB1 Pump with a working pressure of 44 MPa at a flow rate of maximum 2 liters per hour. The pressure drop between the separators E-4 to E-6 can be adjusted by back pressure regulators (TESCOM) to obtain different products and by-products.

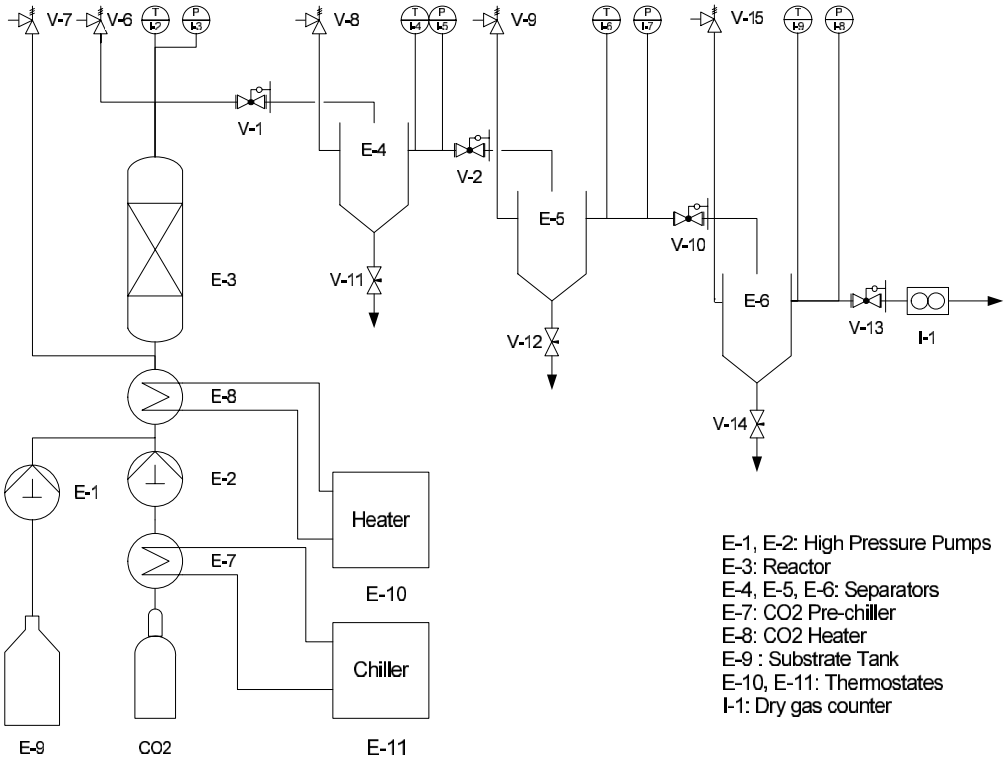

Figure 1: Laboratory scale pilot plant for enzymatic reaction experiments

Transesterification experiments were carried out in the continuously stirred reactor. In the current experiments the substrate containing 25 to 100g of corn oil, 5.2 to 16 g of ethanol and 4 g of immobilized enzyme was given batch wise into the reactor. The reactor was flushed with CO_2 and adjusted to different pressures during the enzymatic reaction. The mixture was stirred at constant temperature and pressure for 18 hours. Afterwards the reaction mixture was extracted by setting on a carbon dioxide flow of about 32 g/min. A pressure of 8.0 MPa was adjusted in Separator E-4 while Separator E-5 and E-6 were operated at 5.0 MPa. The extraction rate was determined by withdrawing samples from the separators and measuring their weight over time. Finally the products in reactor and the separators were analyzed by HPLC.

Analytical Methods

HPLC analysis was carried out on a Waters 600 E Chromatographic system equipped with a Waters 486 UV Detector as well as an Alltech Mk III ELSD. The different species of lipids were analysed after a method of Holcapek et al. [4]. A Waters Symmetry C18 column (WAT 054275) was used, the eluent was fed at 1 ml per minute in a gradient from 100% methanol towards 50% methanol, 22.5% hexane and 27.5% isopropanol over 15 minutes. The conversion of the enzymatic reaction was determined by the decrease of the triglyceride fraction in the samples.

Results and Discussion

Lipozyme–TL showed about the same activity in transesterification experiments under supercritical conditions compared to conventional process conditions. The conversion of triglycerides was found to be around 50% after 18 hours of reaction when an understochiometric amount of ethanol was contained in the substrate. Excess amounts of ethanol diminished the yield. The products could be extracted efficiently at 10 MPa and 40 °C. Setting the first separator (E-4) to 8.0 MPa and 40 °C the extracted material was split into two distinctive fractions. Under these conditions mostly fatty acid ethyl esters were extracted. The second separator contained visible amounts of water next to fatty acid ethyl esters. No significant amounts of extracts were found in Separator E-6.

The products in separator E-4 and E-5 consisted mainly of fatty acid ethyl esters while the reactor contained mainly triglycerides and diglycerides. Peaks with a retention time of 4-5 minutes refer to fatty acids and monoglycerides, fatty acid esters appear between 7 and 9 minutes, diglycerides between 12 and 16 minutes and triglycerides after 20 minutes. The concentration of triglycerides was 2.1% in separator E-4 and 2.7% in separator E-5. Separator E-5 contained visible amounts of water and also ethanol

Conclusions and Outlook

Lipozyme-TL is applicable in supercritical CO_2 as well and led to acceptable reaction yields in first experiments. The concentration of ethanol in the substrate is critical under supercritical conditions as well as in conventional experiments. Excess amounts of ethanol inhibit the enzymatic reaction.

The extraction of fatty acid esters and monoglycerides from the reaction mixture showed to be simple and efficient. So far only two of the three separators have been utilized. A further separation of esters, monoglycerides, and water/ethanol seems possible from the current situation.

In the preceding experiments the reaction rate was too low to allow a simultaneous extraction of the products. The following period of the project it will be focused to enlarge the absolute yield over time in order to accomplish stationary extraction conditions. Next to the optimization of the process it is planned to investigate the behaviour of different oils as well as other enzymes.

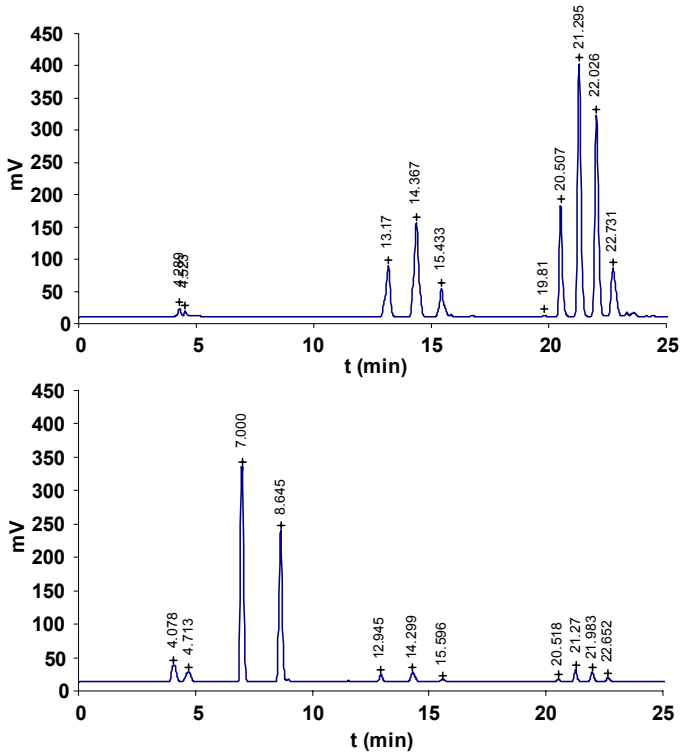

Figure 2: HPLC analysis of the products in the Reactor (top) and Separators E-4 (bottom)

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