Available online at www.sciencedirect.com

ScienceDirect

http://www.elsevier.com/locate/biombioe

# Hydrothermolysis of rapeseed cake in subcritical water. Effect of reaction temperature and holding time on product composition

Hanna Pińkowska [a,*], Paweł Wolak [a], Esther Oliveros [b]

[a] Department of Industrial Chemistry, Wrocław University of Economics, ul. Komandorska 118/120, 53-345 Wrocław, Poland

[b] Laboratoire des IMRCP, UMR CNRS 5623, Université Paul Sabatier (Toulouse III), 31062 Toulouse Cédex 9, France

ARTICLE INFO

*Article history:*
Received 29 September 2011
Received in revised form
7 November 2013
Accepted 14 March 2014
Available online 14 April 2014

*Keywords:*
Rapeseed cake
Subcritical water
Hydrolysis
Amino acids
Fatty acids
Experimental design methodology

ABSTRACT

We have investigated the hydrothermolysis of rapeseed cake, which is a residual biomass with high protein and fat content. The effects of the process parameters, reaction temperature and holding time, on the composition of the products (amino acids and fatty acids) contained in the separated liquid fractions (water and ether, respectively) were studied. To model the hydrothermal process the experimental design methodology was used. Based on this, optimized operational parameters were determined yielding highest amounts of amino acids and high conversion of triacylglycerols to fatty acids. A maximum estimated yield of amino acids of 135.9 g kg-1 of rapeseed cake was obtained at 215 °C after 36 min. A further increase of both reaction temperature and holding time would lead to the Maillard reaction and the decomposition (deamination and decarboxylation) of the amino acids. Maximum conversion of triacylglycerols to fatty acids of 0.91 was predited at 246 °C during 65 min. In this case, a further increase of both reaction parameters would lead to enhanced cis–trans isomerization of the unsaturated fatty acids produced.



## 1. Introduction

Rapeseed cake is a residual biomass from the pressing of oil from rapeseed. From the processing of rapeseed large amounts of rapeseed cake are released as by-product (about 650 kg from 1 t of rapeseed). Poland is one of the major rapeseed (*Brassica napus* L.) producers in Europe and the rapeseed growing area is forecast to further increase in the years to come. Rapeseed cake has a high protein and fat content. Traditionally, rapeseed cake has been applied as a livestock feed. However, the forecasted increase in rapeseed oil production may cause difficulties in the agricultural application of rapeseed cake.

For several years, research into rapeseed cake through thermochemical processing, e.g. pyrolysis yielding bio-oil and biocarbon [1,2], catalytic conversion producing bio-oil [3,4], and co-combustion with hard coal [5], has been conducted worldwide. However, these utilization methods do not allow recovery of the valuable components of the residual biomass, which is possible by using hydrothermal processes conducted in subcritical water. Due to its special properties [6–8], most

* *Corresponding author*. Tel./fax: +48 71 368 0275.
E-mail address: hanna.pinkowska@ue.wroc.pl (H. Pińkowska).
http://dx.doi.org/10.1016/j.biombioe.2014.03.028
0961-9534/

biomass raw materials may be easily hydrolysed to many valuable feedstocks, among them to amino acids and fatty acids.

Depending on the biomass composition the hydrothermal processes of biomass treatment may lead to only amino acids, only fatty acids or mixtures which after separation give both products: aqueous phase containing amino acids and oil phase, rich in fatty acids [9–12]. Recently there was efficiently performed the hydrothermolysis of protein wastes derived from meal processing industry [13–15], seafood industry [16–21], brewery industry [22], silk industry [23] and also other raw materials rich in proteins such as bovine serum albumin [24] and whey protein isolate [25], sewage sludge [19], baby food [26], rice bran [27–30], soybean meal [28], bean dregs [31], microalgae [32,33], raw grass clippings [34] and water lettuce [35]. Several attempts also have been made at the hydrothermolysis of a fat-rich resources: vegetable oils [36–43], squid wastes [20,44], fish meal (horse mackerel) [16] and microalgae [45], which resulted in saturated, monoenic, dienic and polyenic fatty acids, including long chain polyunsaturated acids. In turn the conversion of scallop viscera wastes and squid entrails in a two-step process allowed production of separated fractions: rich in amino acids and fatty acids [43,46].

The hydrothermal methods (under subcritical conditions) have many advantages in relation to traditional methods of amino acids and fatty acids production based on chemical and microbiological syntheses, which are complicated, expensive, require toxic reagents and cause many purification problems. In contrast hydrothermal technologies do not require the addition and recovery of chemicals except for water in consequence allowing valuable materials to be produced with zero emissions [46]. The drying of raw material is not required which makes the process energy saving. Due to high-temperature, high-pressure conditions and the catalytic properties of water arising from its high ionic product under hydrothermal conditions, reactions are faster and may be easily controlled by temperature and pressure adjustment [13,34]. Also lower dielectric constant, viscosity and surface tension of subcritical water enhance the solubilization of treated raw materials and transport of the reagents which accelerate the reaction rates [6,7,13]. Other advantages of hydrothermal processes are limited equipment corrosion problems and simple operation [47]. Considering the above, hydrothermal processes are regarded as environmental friendly, cost effective and having a great potential for practical applications.

Since investigations of rapeseed cake hydrothermolysis are rare (to the best of our knowledge no report has been published) herein we propose a hydrothermal path for rapeseed cake treatment yielding a liquid fraction rich in amino acids and fatty acids as an alternative method of its utilization. This study focuses on the effects of the reaction temperature and time of hydrothermolysis of rapeseed cake, as a first step towards a mechanistic interpretation and an evaluation of the feasibility of its technical development. The optimal experimental design (OED) methodology was used to establish a statistically significant reaction model as well as for optimizing the conditions for amino acids and fatty acids production.

## 2. Materials and methods

### 2.1. Materials and chemicals

Rapeseed cake was obtained from the Wilmar Oil Press Plant in Żórawina (the Lower Silesian Province, Poland). The moist material was dried to constant mass at a temperature of 103 °C and ground to a grain size of below 1 mm. All solvents and reagents were purchased from Sigma–Aldrich and Fluka (amino acids). Depending on the requirements of the particular analytical or investigative method, analytically or HPLC-pure reagents were used.

### 2.2. Reactor and experimental procedure

The hydrothermolysis of rapeseed cake was performed in a batch reactor (4576A, Parr Instrument Company, USA). A detailed description of the reactor equipment, as well a schematic diagram of experimental set-up (Fig. 1S), is given in Supplementary material.

The investigation of hydrothermolysis of rapeseed cake was conduced in two stages. The aim of the first preliminary stage was to establish the range of temperature and holding time of hydrothermolysis of the raw material conversion to amino acids and fatty acids with significant yield. On the basis of these results the optimal experimental design was applied in two experimental series for optimization of amino acids (series 1) and fatty acids (series 2) production, which was the second stage of the study.

In preliminary study the hydrothermolysis of the rapeseed cake was conducted at a reaction temperature ($T$) of 180, 200, 220, 240, 260 and 280 °C. The reaction would be stopped once the intended temperature was reached (zero holding time), and after a holding time ($t$) of 5, 10, 20, 30, 40 and 60 min. In all experiments the pressure corresponded to the vapour pressure curve at the given temperature, or slightly exceeded it (at 180 °C–1.23 MPa, 200 °C–1.85 MPa, 220 °C–2.88 MPa, 240 °C–4.14 MPa, 260 °C–5.52 MPa, 280 °C–7.45 MPa).

In the second stage of the study two series of designed experiments were performed in which reaction temperature and holding time were varied simultaneously: in experimental series 1, rapeseed cake hydrothermolysis was performed at temperature ranging from 180 to 240 °C and holding time from 0 to 60 min, whereas in series 2, temperature varied from 200 to 260 °C and holding time from 0 to 80 min. The experimental conditions are given in Supplementary Material (Table 1S).

For each hydrothermolysis experiment, HPLC-pure water was subjected to degasification in an ultrasonic bath and purged with nitrogen. Rapeseed cake (10 g) in water (90 g) suspension was introduced into the reaction vessel, preheated to about 80 °C. The reactor was closed and the reaction vessel with its content was purged with nitrogen under a pressure of 2 MPa and heated up at a rate of 10–15 °C $min^{-1}$ to a predetermined temperature for 10–15 min, and kept at this temperature with an accuracy of ±1 °C. The time during which the reaction mixture components were kept at the prescribed temperature was considered as the reaction time (holding time). When the reaction was over, the reaction vessel was