# ADVANCES IN RESEARCH AND TECHNOLOGY OF RAPESEED OIL

## Monograph – part II

Wydawnictwo Naukowe Uniwersytetu Mikołaja Kopernika
Toruń 2009



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ISBN 978-83-231-2452-8

Printed in Poland


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Wydanie I.
Druk: Drukarnia Cyfrowa UMK
ul. Gagarina 5, 87-100 Toruń

# LOW-*trans* PARTIALLY HYDROGENATED RAPESEED OIL FROM ELECTROCHEMICAL MEMBRANE REACTOR

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***Abstract***

Rapeseed oil has been hydrogenated electrochemically in the proton-exchange membrane reactor with two different commercial membranes (Nafion 110 and Fumapem F-1030) over palladium black catalyst at temperature 50-70°C. *Trans* fatty acid content in the obtained partially hydrogenated product was in the range of 0-2%.

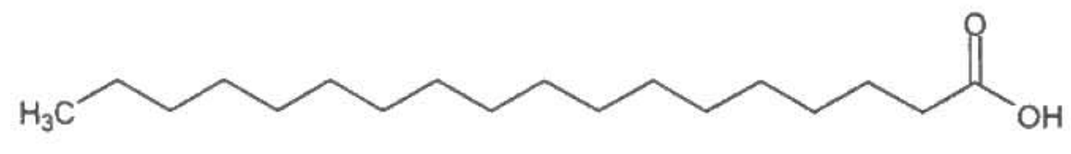
***Key words***: rapeseed oil, electrochemical hydrogenation, proton-exchange membrane, *trans* fatty acids

## *INTRODUCTION*

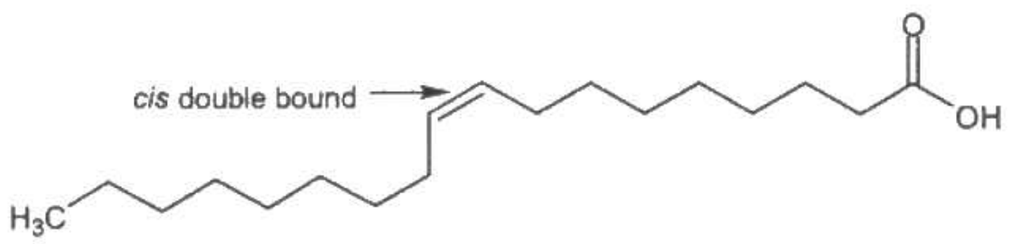
Most vegetable oils, including rapeseed (*Brassica napus* L.), contain low percentage of saturated fatty acids and high percentage of unsaturated fatty acids that have their double bonds in the cis configuration (Table 1, Fig. 1).

Hydrogenation of unsaturated fatty acids is one of the earliest and most important industrial processes for the modification of vegetable oils. The aim of this process is to convert liquid oils into semisolid or solid fats with desired melting characteristics and improved oxidative and thermal stability. Conventional chemical hydrogenation is usually carried out in semi batch reactor over a nickel catalyst suspended in the liquid oil and hydrogen gas is supplied. Since this process is not effective at low temperatures, it is conducted at temperature in the range of 150-225°C. Unfortunately, high reaction temperatures promote the production of fatty acids in the form of *trans* isomers (TFA) (Fig. 2). There is a number of papers

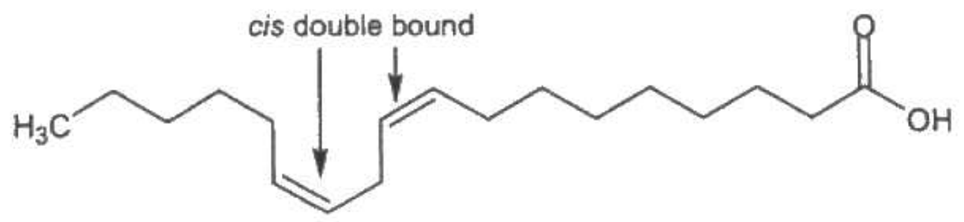
describing the effects of these compounds for human health. It results from them, that TFA increase low-density lipoprotein (LDL, bad) cholesterol levels and also reduce high-density lipoprotein (HDL, good) cholesterol levels [1]. It has been also confirmed, that *trans* fats inhibit the metabolic conversion of linoleic acid to arachidonic acid, which is essential for normal children growth and development [2]. Therefore many countries have introduced or intend to introduce the strict regulations on TFA content in food. Hence, there is considerable industrial interest in development of hydrogenation methods alternative to high *trans*-producing conventional ones. The most popular alternatives include processes based on supercritical [3, 4] and electrochemical technology. Electrochemical hydrogenation of vegetable oils have been examined using two different ways to transfer hydrogen to the oil: a mediator-assisted approach [5] or a method employs a proton-exchange membrane [6]. These studies have demonstrated that electrochemical hydrogenation results in *trans* fatty acid formation much lower than in the case of conventional method.



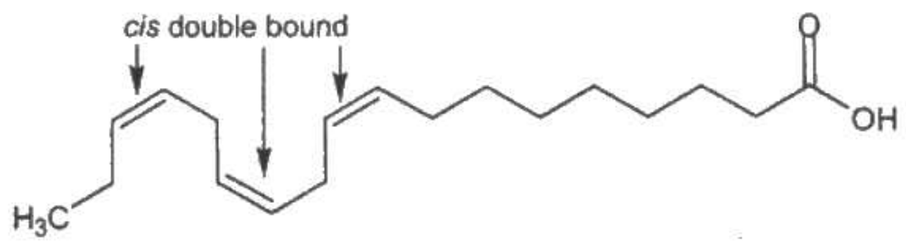

Stearic acid C 18:0




Oleic acid C 18:1



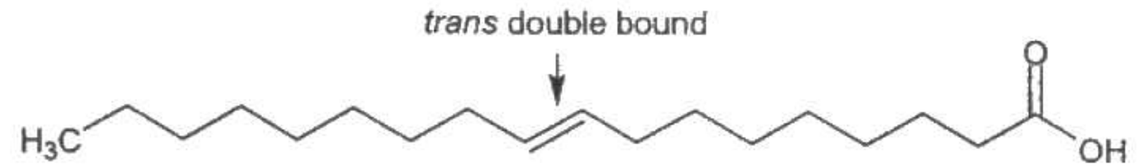

Linoleic acid C 18:2



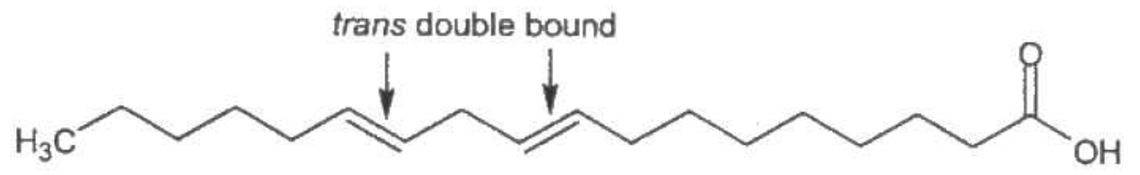

Linolenic acid C 18:3

**Fig 1.** Chemical structure of the most common fatty acids present in vegetable oils






Elaidic acid C 18:1




Linoleladic acid C 18:2

**Fig. 2**. Chemical structure of *trans* fatty acids present in partially hydrogenated product

Here we demonstrate the electrochemical hydrogenation of rapeseed oil by using a proton-exchange membrane (PEM) reactor with two different commercial membranes (Nafion 110 and Fumapem F-1030) over palladium black catalyst at temperatures ranging from 50 to 70°C. Our results indicate that it is possible to obtain a partially hydrogenated product with *trans* fatty acids content about 1% or even below detectable limit *using reaction conditions mentioned above*.

## *MATERIALS AND METHODS*

### *Proton-exchange membrane reactor*

Hydrogenation process was carried out in PEM reactor, shown schematically in Fig. 3. The main part of the reactor is membrane-electrode-assembly (MEA). It was prepared as follows: Pd-black catalyst (Aldrich) was dispersed in

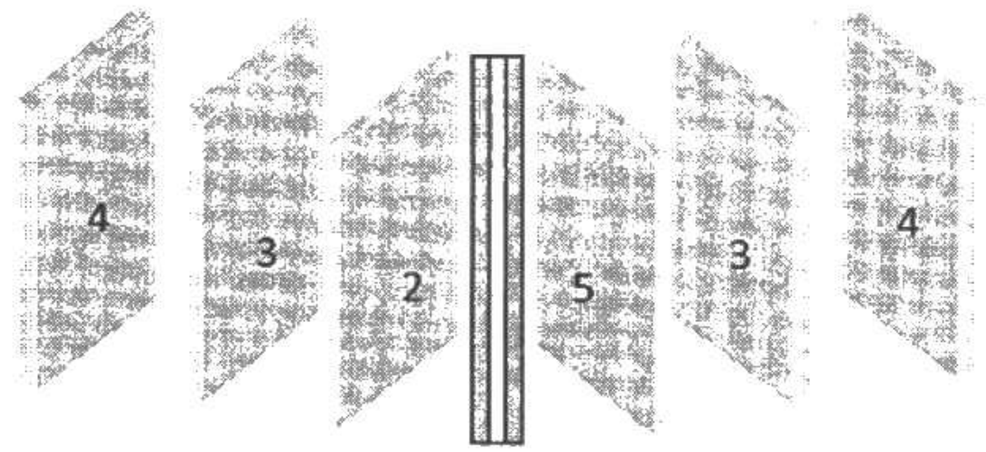



**Fig. 3.** Schematic diagram of PEM reactor; 1 - MEA, 2 - stainless steel plate with patterned flow channel, 3 - thermostatting block, 4 - stainless steel plate, 5 - teflon plate with patterned flow channel

5 wt% Nafion® solution (DuPont, USA) or 5 wt% Fumion® solution (FuMA-Tech GmbH, Germany) and coated on the carbon paper (Toray). Next, this paper was hot-pressed at ca. 120°C for 90 s under a pressure 160 atm with Nafion® 110 (DuPont, USA) or Fumapem® F-1050 (FuMA-Tech GmbH, Germany) cation-exchange membrane. In another experiments, carbon paper was not used but membrane Nafion was stuck to the stainless steel mesh using Fumion solution.

### *Oil hydrogenation experiments*

A schematic representation of the electrochemical processes taking place in PEM reactor is shown in Fig. 4. The water is electrolyzed at the anode to oxygen gas, hydrogen ions and electrons. The hydrogen ions flow across the cation-exchange membrane to the catalitically active cathode surface where they are reduced to hydrogen atoms. Finally, addition of hydrogen atoms to the double bonds of unsaturated fatty acids takes place.

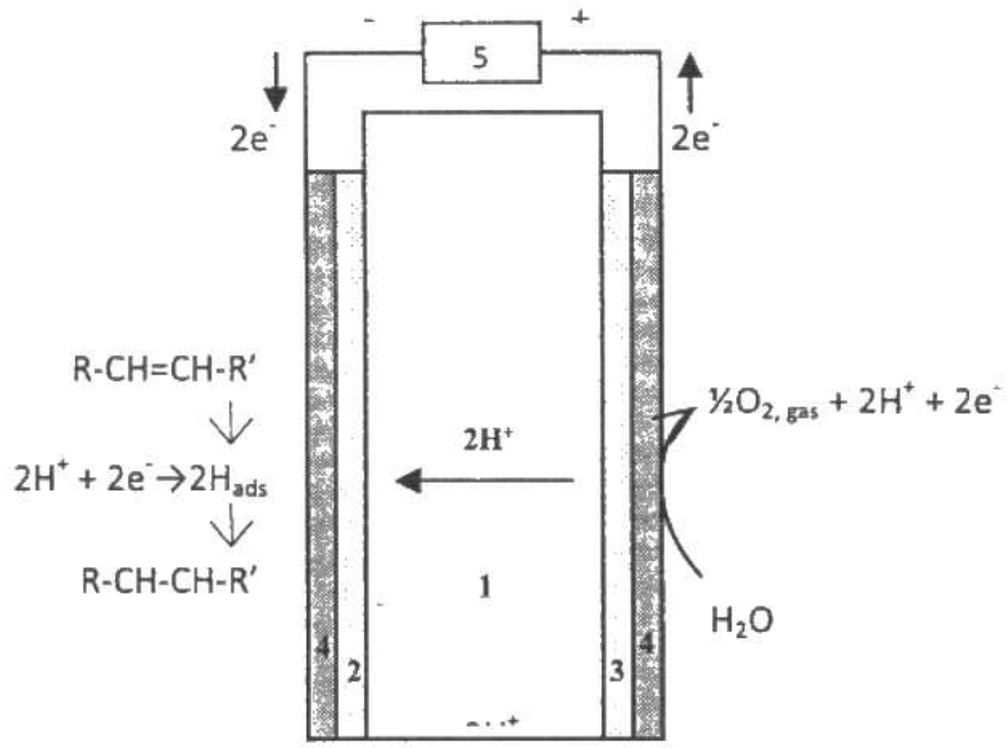



**Fig. 4.** Schematic representation of the electrochemical reactions taking place in PEM reactor; 1- proton conducting cation-exchange membrane, 2 - cathode catalyst, 3 - anode catalyst, 4 - carbon paper or stainless steel mesh, 5 - direct current power supply

The hydrogenation was carried out at a constant applied current density of 12.5 mA/cm$^2$ and temperatures 50, 55, 60, 65 and 70°C. The duration of each run was 5-6 h. In all experiments bleached rapeseed oil (Bunge Company, Poland) was used.



### *Products analyses*

Fatty acid compositions of the initial oil and the partially hydrogenated products were determined by gas chromatographic analysis. The iodine value (IV) was calculated from the composition obtained by GC analysis using Eq. 1 [7].

IV = (1% hexadecenoic acid × 0.950)+ (1% octadecenoic acid × 0.860)
+ (% octadecadienoic acid × 1.732)+ (% octadecatrienoic acid × 2.616)
+ (% eicosenoic acid × 0.785)+ (% docosenoic acid × 0.723)

## *RESULTS AND DISCUSSION*

Fatty acid profiles and iodine values of rapeseed oil and the partially hydrogenated products are listed in Table 1. As expected, there is an increase in the concentration of stearic acid (C 18:0) and elaidic acid (C 18:1 *trans*) and

**Table 1.** Selected results (%) of partial hydrogenation of rapessed oil in PEM reactor[a]; the Roman numerals denote experimental runs

| Fatty acid | Starting oil | I[b] | II | III | IV | V[c] | VI[d] | VII[e] | VIII[e] | IX[e] | X[e] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **C 14:0** | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| **C 16:0** | 4.5 | 4.5 | 4.7 | 4.6 | 4.6 | 4.8 | 4.6 | 4.7 | 4.7 | 4.7 | 4.6 |
| **C 16:1** | 1.1 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| **C 18:0** | 1.8 | 9.4 | 7.8 | 7.4 | 8.2 | 9.4 | 7.1 | 8.7 | 9.4 | 8.7 | 7.9 |
| C 18:1 trans | | 0.5 | 0.5 | 0.6 | 0.7 | 0.9 | 0.4 | 0.8 | 1.7 | 1.4 | 1.2 |
| **C 18:1** | 60.9 | 56.7 | 57.6 | 57.9 | 57.4 | 56.8 | 58.1 | 57.4 | 57.2 | 57.7 | 58.0 |
| **C 18:2 trans** | | 0.0 | | 0.0 | 0.1 | 0.1 | | 0.1 | 0.2 | 0.2 | 0.1 |
| **C 18:2** | 19.2 | 17.4 | 17.9 | 17.9 | 17.8 | 17.3 | 17.9 | 17.4 | 17.1 | 17.3 | 17.6 |
| **C 18:3 trans** | | 0.1 | | 0.1 | 0.0 | 0.0 | | 0.1 | 0.2 | 0.2 | 0.2 |
| **C 18:3** | 9.5 | 8.6 | 8.6 | 8.9 | 8.7 | 8.4 | 8.8 | 8.5 | 8.4 | 8.4 | 8.6 |
| **C 20:0** | 0.6 | 0.8 | 0.8 | 0.8 | 0.8 | 0.9 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| **C 20:1** | 1.5 | 1.5 | 1.5 | 1.5 | 1.4 | 1.3 | 1.6 | 1.4 | 1.4 | 1.4 | 1.4 |
| **C 22:0** | 0.3 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| **C 22:1** | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.5 | 0.4 | 0.4 | 0.4 | 0.4 |
| **SFA** | 7.3 | 15.2 | 13.7 | 13.2 | 14.1 | 15.6 | 13.0 | 14.7 | 15.3 | 14.7 | 13.8 |
| **TFA** | 0.0 | 0.6 | 0.5 | 0.8 | 0.7 | 1.1 | 0.4 | 1.0 | 2.0 | 1.8 | 1.5 |
| **IV** | 113.1 | 103.0 | 104.8 | 105.6 | 104.5 | 102.2 | 105.8 | 103.3 | 102.3 | 103.0 | 104.4 |

[a] MEA: Pd-loaded carbon paper hot-pressed to the Nafion 110 membrane, 12.5 mA/cm$^2$ current density, 60°C temperature, time: 5-6 h.
[b] Membrane Fumapem was used.
[c] The flow was reduced by half.
[d] A stainless steel mesh was placed between the membrane and the cathode compartment.
[e] Carbon paper was not used but membrane Nafion was stuck to the stainless steel mesh using Fumion solution.

a decrease in the concentration of linoleic acid (C 18:2 *cis*) and linolenic acid (C 18:3 *cis*). The *trans* fatty acids contents in hydrogenated oil products ranged from 0.4 to 2.0% whereas the iodine values (defined as the number of grams of iodine bound per 100 g of fat and indicate the level of hydrogenation) are in the range of 102.2 to 105.8. For comparison, in the conventional hydrogenation process of rapeseed oil with nickel catalyst 29.5 and 19.7% TFA were formed at an IV of 102.7 and 104.8, respectively [8]. Thus, the significant reduction in TFA content was achieved using the electrochemical hydrogenation method.

### *Effect of temperature*

The efect of temperature on the total TFA content in partially hydrogenated rapeseed oil is shown in Fig. 5. As it is seen, with increasing the reaction temperature from 50 to 70°C the TFA concentration in the hydrogenation product increases from 0% to ca. 1%. Fig. 6 displays the curves of iodine value as a function of the temperature. When the temperature of hydrogenation was increased the corresponding iodine value of the hydrogenated rapeseed oil was found to decrease. The results shown in these two figures clearly indicate that the temperature under which the hydrogenation process took place was not only associated with increasing concentration of TFA in the final product but also the extent of the reaction, as evidenced by the iodine value.

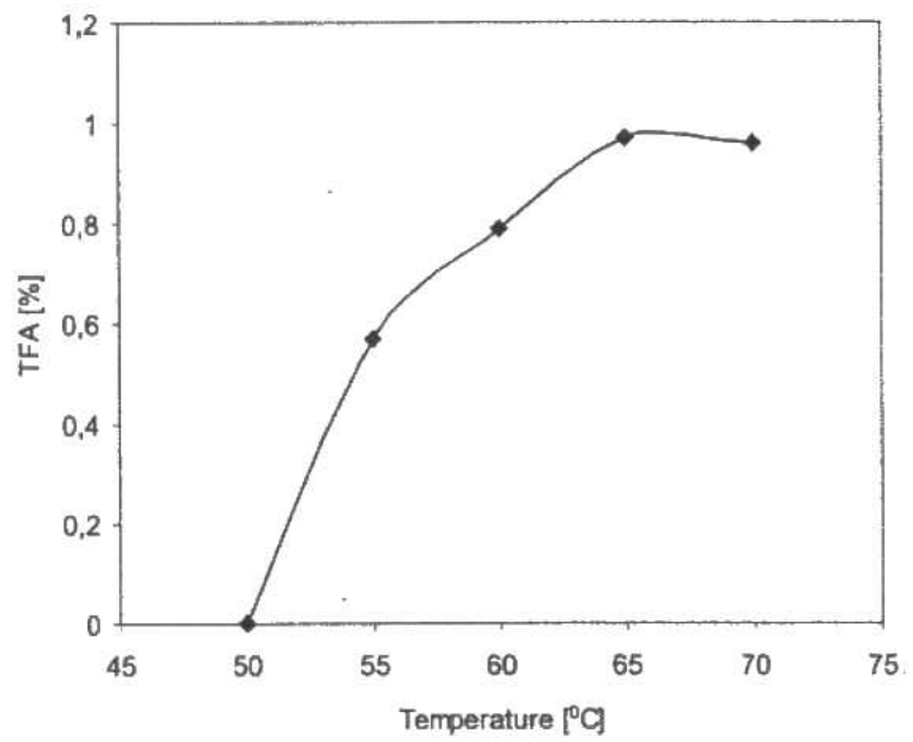



**Fig. 5.** Effect of temperature on the total TFA content in partially hydrogenated rapeseed oil



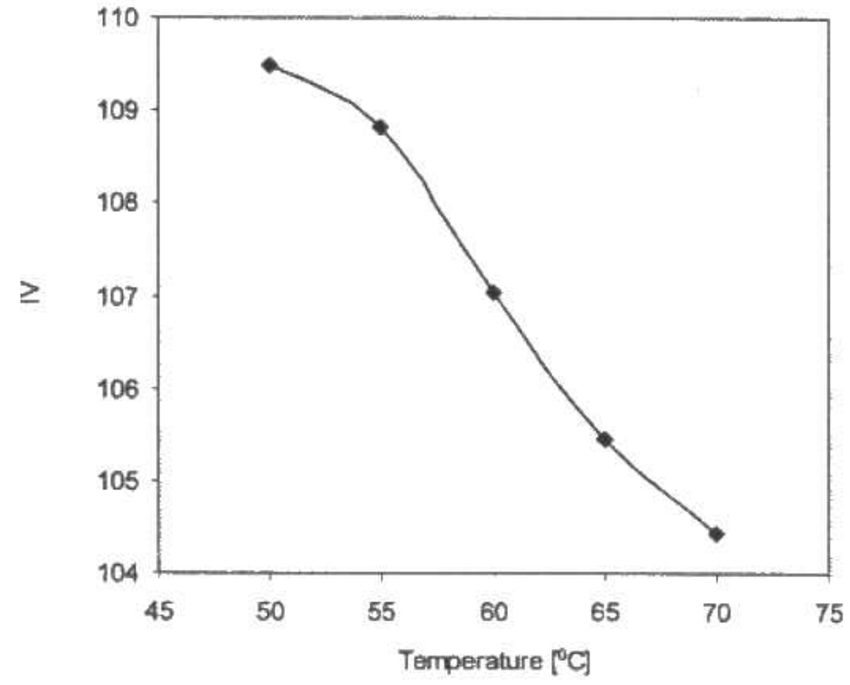



**Fig. 6.** Iodine value (IV) of the partially hydrogenated rapeseed oil products as a function of hydrogenation temperature

## *CONCLUSIONS*

According to our experiments the partially hydrogenated rapeseed oil with an iodine value about 103 can be prepared by electrochemical hydrogenation at moderate temperature and at atmospheric pressure in proton-exchange membrane reactor using Pd-black as a catalyst. Generally, the electrochemical method leads to the formation of significantly lower amounts of TFA (0-2%) compared to the traditional method with nickel catalyst. We also found that the concentration of TFA in the reaction products depends on the temperature: TFA content increases with the reaction temperature. The further investigations will be focused on development of the proton-exchange membrane reactors with membranes cheaper than perfluorinated Nafion membrane.

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# *YELLOW-SEEDED RAPESEED – RECENT ADVANCEMENTS IN RESEARCH AND BREEDING*

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***Abstract***

The increasing demand for rapeseed oil production generates large quantities of rapeseed meal and mill cake remaining after the extraction. These in turn are valuable high protein content feedstuff. This creates a need to eliminate the adverse characters of rapeseed, for example, large presence of dietary fiber. The solution seems to be a development of yellowseeded rapeseed varieties. Molecular characterization of lines developed in PBAI and the identification of essential genes and QTLs using molecular markers coupled with the color of seeds/fiber content allows to carry out molecular markers assisted selection (MAS) for further breeding and improvement of the material. The development of selective markers is necessary due to the needs of efficient and modern breeding varieties of double low yellowseeded rapeseed. The inheritance of this trait has been already investigated. The development of such varieties is one of the strategic objectives of research and rapeseed breeding.

***Key words***: yellowseedness, fibre, content of fat and protein, molecular markers, genetic mapping, Marker Assisted Selection (MAS)

## *INTRODUCTION*

The valid and still growing role that winter rapeseed plays in the world as a source of nutrition for human consumption and feeding livestock as well as a source of energy for industrial and transport purposes makes necessary the continuous genetic and breeding research aimed at quality of rapeseed, to improve it and adjust seeds to consumer needs. Until now significant progress in yielding capacity has been successfully achieved, in recent years mainly by the introduction of high yielding of open pollinated and hybrid varieties. Previously the varieties characterized by high content of harmful compounds like eruic acid and glucosinolates were created [1, 2]. This double low (00) or *canola* named rapeseed gives healthier, tastier oil and more valuable fodder for livestock.