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Evaluation of chosen quality parameters of used frying rape oil as fuel biocomponent

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A b s t r a c t. In this paper higher fatty acids composition, peroxide and acidic value and density of raw commercial rape oil and of oil fraction formed after each of five cycles of oil heating conducted in two ways - with and without potato chips frying, were compared. After each heating, which duration corresponded to time necessary for potato chips frying, oil was left to cool down (to room temperature) and stored in conditions similar to ones found in small gastronomy.

Goal of undertaken research was usability assessment of used frying rape oil as a substrate for biofuel production. Utilization of used frying rape oil as fuel seems to be grounded by favourable ratio of saturated and unsaturated fatty acids in oil fraction, which properties stabilize as a result of surface contact with potato chips, as well as by ecological (utilization of waste), energetic (replacement of conventional crude oil based fuels) and economical (utilization of cheap wastes) reasons.

K e y w o r d s: rape oil, used frying oil, fatty acids composition, acidic value, peroxide number, fuel biocomponent

INTRODUCTION

Degradation of plant oils used in small gastronomy for food preparation is going in a few directions. Kinetic of changes is bonded with structure and chemical properties of oil, especially glycerol estrification and number of double bonds in higher fatty acids (Sikorski, 2000; Tys *et al*., 2003), high temperature and access of sunlight, which all trigger generation of free radicals and favor free-radical chain transformations (Choe and Min, 2006).

It is also bonded with a numerous precursors, among which the most important are: atmospheric oxygen with oxidation catalysts like heavy metals (iron, cooper, cobalt, chrome) (Sikorski, 2000; Choe and Min, 2006), but also, present in raw material, water which has, in presence of some substances added to food (soda, emulgators and baking powder) and remains of substances used to clean frying equipment (detergents, caustic soda), hydrolytic influence (Blumenthal, 1991).

High content of oxygen dissolved in oil favors its reactions with double bonds of fatty acids and creation of hydroperoxides – precursors of numerous processes generating substrates of free-radical oxidation transformations (Choe and Min, 2006; Sikorski, 2000), and, as a result of molecule breakdown, alcohols, aldehydes and short-chain fatty acids. At the same time dehydration may lead to formation of ketones (Valdes and Garcia, 2006).

In deeper layers of oil, to which access of oxygen is limited, dominating changes are ones leading to generation of free radicals (as a result of thermal cracking), which are precursors of polymerization changes of oil. Formation of these polymers results with macroscopically noticeable changes in density and consistency of fat (Paul and Mittal, 1996; Sikorski, 2000).

Water getting into oil with detergents, emulgators and caustic soda is an environment for hydrolytic changes of oil. It favors increase of oil acidic value (Clark and Serbia, 1991), secondary oxidation changes of dehydrolyzed fatty acids and transestrification of fat (Jacobson, 1991).

Properties of degraded used frying oil after it gets into sewage system are conductive to corrosion of metal and concrete elements. It also affects installations in waste water treatment plants. Fat covering elements of installations and therefore reducing flow in them decreases their efficiency, at the same time increases cost of their operation.

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Proper management of used frying oils from gastronomy is an increasing ecological and economical problem, which can be solved through utilization of these wastes for purpose of fuel production.

Goal of undertaken research was evaluation of chosen properties, especially usability for biofuel production, of fresh commercial rape oil compared to oil fractions formed after each of five cycles of heating of this oil and during potato chips frying.

MATERIALS AND METHODS

Five litres of rape oil from commercially sold batch was purchased as five containers 1l each and used in this research. Their content was poured into one container and mixed. Obtained mixture was called 'raw rape oil' and brought to temperature of 20°C prior to areometric density analysis, after which, sample to be used in further laboratory research was taken. Remaining oil was heated up to temperature enabling frying chips, which were made of commercially available raw potatoes, cut to the shape and size of available in trade frozen chips. After frying and removing potato chips, oil was left in the container to cool down to room temperature. When it reached 20°C areometric density analysis was conducted. Remaining amount of oil fraction was covered with laboratory blotting paper and left in room temperature for 24 h. After that sample called 'heating 1' was taken for further laboratory analyses. 24 h later, oil fraction was heated up with chips and described above actions were repeated – in this way sample called 'heating 2' was obtained. The cycles embracing heating, cooling, density analysis and sampling were repeated and samples labeled 3, 4 and 5 were taken.

In order to investigate effect of chips frying on results of oil fraction analyses similar cycles of rape oil heating and cooling (heating 1-5) were conducted without use of chips.

Each of taken laboratory samples of oil undergone analysis of acidic (PN-ISO 660 – 1998) and peroxide (PN-ISO 3960 – 1996) number as well as of fatty acids composition (Krełowska-Kułas, 1993).

Determination of fatty acids composition was conduced by means of method based on use of gas chromatography. Extracted fat had undergone alkali hydrolysis, after which fatty acids were brought in to methyl esters, which were than separated on chromatographic column and their content in sum of fatty acids was found.

RESULTS AND DISCUSSION

Raw rape oil characterized with typical properties meeting quality norms (PN-A-86908) for product in trade – peroxide number =1.54 $mM_O\ kg^{-1}$ (Fig. 1) and acidic value = 0.2 mg KOH g^{-1} (Fig. 2). Oil was clear without sediments – in accordance with PN-A-86908 (2000) and its density was 0.918 g cm^{-3}.

Fatty acids composition of trade oil was typical for ripe seeds of non-erucic rape variety (PN-A-86908), containing 7.22% of saturated fatty acids (0.12% myristic – C_{14}^{0}, 5.31% palmitic – C_{16}^{0} and 1.79% stearic – C_{18}^{0}) and 92.65% of unsaturated fatty acids, among which greatest amounts of oleinic – C_{18}^{1} (60.63%), linoleic – C_{18}^{2} (22.27%) and linolenic – C_{18}^{3} (9.75%) were noted.

Heating of rape oil in laboratory conditions (small container in which the experiment was carried out and free access of air) caused significant, characteristic mainly for

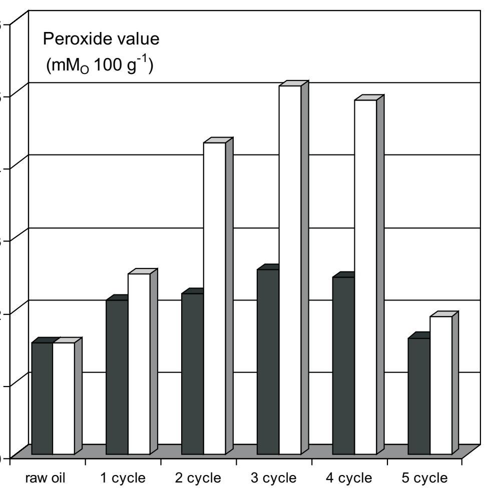


Fig. 1. Peroxide value of oil subjected to cyclic heating (mM_O 100 g^{-1}). ■– oil heated in presence of potato chips, □ – oil heated without presence of potato chips.

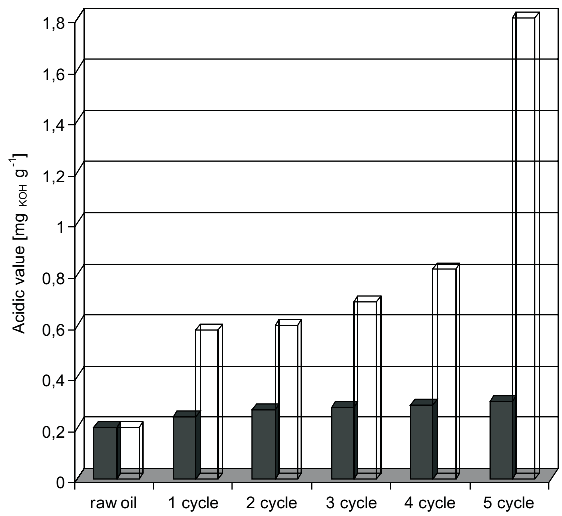
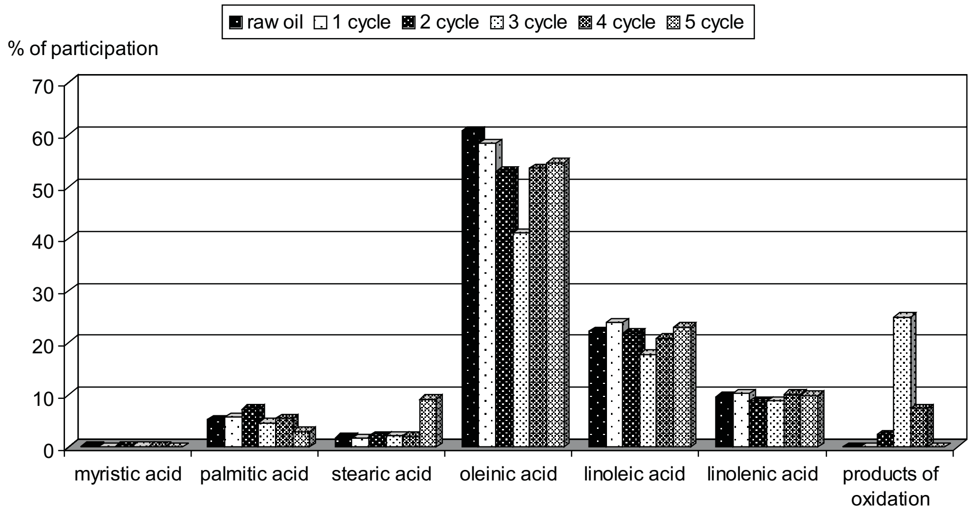


Fig. 2. Acidic value of rape oil subjected to cyclic heating (mg KOH g^{-1}). Explanations as on Fig. 1.

a



b

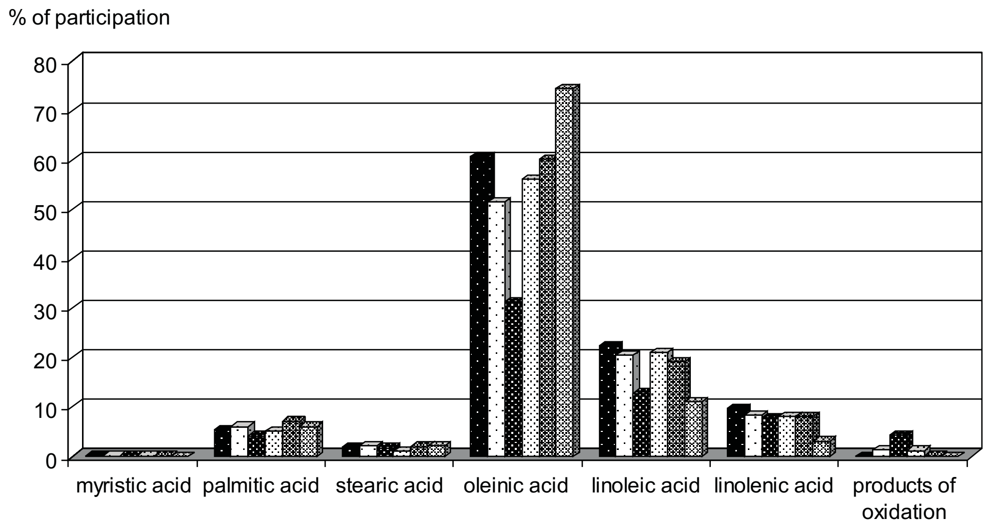


Fig. 3. Participation of particular fatty acids (%). In rape oil subjected to heating: a – during potato chips frying, b – without presence of potato chips.

oxidation processes, changes of fatty acids composition (Jacobson, 1991; Valdes and Garcia, 2006), (Fig. 3a,b). Polymerization transformations of investigated rape oil were probably of less significance, what was suggested mainly by small fluctuations of oil density during the experiment.

It varied from observed at the beginning of experiment 0.918 to 0.917 g cm^{-3} in the first and the second cycle and 0.918 g cm^{-3} in the third and the fourth one, to reach finally 0.919 g cm^{-3} in the fifth cycle.

Characteristic property of oxidation transformations is mainly significant initial decrease of unsaturated fatty acids content (observed maximally up to third heating cycle) with simultaneous increase of products of partial fat oxidation content and increase of peroxide number value – (Fig. 1). Peroxide number (LN) in tested oil for chips frying was at the level of 1.54-2.56 mM_O 100 g^{-1}, while in oil heated without chips – 1.54-5.09 mM_O 100 g^{-1}, and it reached its maximum values after the third heating cycle. Peroxide number in oil heated with and without chips gradually increased up to the third cycle, whereas it decreased after the fourth and fifth heating cycles. Changes of peroxide number were higher in oil heated without chips.

Characteristic feature of these transformations is likely catalytic behaviour of chips, which manifested through significantly higher participation of partial oxidation products in oil which had contact with chips, when compared to analogical samples heated without chips (Fig. 3a, b), as well as probable sorption of oxidation products by chips what is indicated by decrease of peroxide number of samples heated in presence of chips (Fig. 1).

Acidic number (LK) in tested oil for chips frying was at the level of 0.2-0.34 mg KOH g^{-1} of fat. Values of LK gradually increased along with the frying cycles reaching 50% increase in relation to raw oil in the fifth cycle. In oil heated without chips, acidic number (LK) varied from 0.2 to 1.8 mg KOH kg^{-1} of fat, while significant changes of acidic number occurred after the first heating cycle (almost 3-fold increase) as well as after the fifth cycle (almost 2-fold increase) as compared to LK after the fourth and almost 10-fold increase comparing to raw rapeseed oil.

Acidic value of investigated oil was increasing systematically during heating without contact with potato chips (Fig. 2). This phenomenon also indicates on oxidation profile of oil transformations, because samples, from the same heating cycle, heated with chips characterized with lower values of acidicvalue.

It might result from marginal effect of hydrolytic transformations of oil (related mainly with water fraction getting into oil with potato chips).

Analysis of results presented in Fig. 3a, b revealed that the decrease of polyunsaturated fatty acids content occurred in oil heated without chips. Levels of unsaturated fatty acids in raw oil decreased up to the third heating cycle, and then it increased.

As a result of five cycles of oil heating during frying potato chips, oil containing similar amount of fatty acids as raw material (fulfilling requirements of PN-A-86908, 2000) was obtained. The presence of potato chips in post-frying oil stabilized the unsaturated fatty acids profile. Heating oil without chips caused significantly greater differences in omposition of fatty acids, especially when unsaturated fatty acids are taken into consideration, therefore utilization of such oil as a substrate for biofuel production might be more difficult.

Rape oil after five cycles of heating characterized with increased acidic value, what might cause difficulties during biofuel production, because one of its stages is a process of alkali hydrolysis, in which such oil is neutralized. However it should not be a barrier when it is to be combusted in an engine (Alonso *et al*., 2002; Staat and Vallet, 1994).

Undertaken research suggests that utilization of used plant oils for fuel production seems to be possible, however requires further research on material obtained from gastronomy, especially in order to investigate its usefulness and energetic efficiency of its combustion.

CONCLUSIONS

1. Obtained results of research on used frying oils allow assumption that they can be used for production of biofuel to be combusted in engines. It seems that the only weak point of such oil is increased acidic value what might cause difficulties during biofuel production, because one of its stages is a process of alkali hydrolysis, in which such oil is neutralized. However, it should not be a barrier when it is to be combusted in an engine.

2. Utilization of rape oil used for frying as fuel seems to be justified when favourable ratio of saturated and unsaturated fatty acids in oil fraction, which is the property that stabilizes as a result of surface contact with potato chips, is taken into consideration. Also ecological (utilization of wastes) and economical (partial substituting of conventional crude oil based fuels) are not to be omitted.

REFERENCES

Alonso M.I., Valdes A.F., Martinez-Tarazona M.R., and Garcia A.B., 2002. Coal recovery from fines cleaning wastes by agglomeration with colza oil: a contribution to the enviroment and energy preservation. Fuel Proces. Technol., 75, 85-95.

Blumenthal M.M., 1991. A new look at the chemistry and physics of deep-fat frying. Food Technol., 45(2), 68-94.

Choe E. and Min D.B., 2006. Mechanisms and factors for edible oil oxidation. Comprehensive Reviews in Food Science and Food Safety, 5, 169-186.

Clark W.L. and Serbia G.W., 1991. Safety aspects of frying fats and oils. Food Technol., 45(2), 84-94.

Jacobson G.A., 1991. Quality control in deep-fat frying operations. Food Technol., 45(2), 72-74.

Krełowska-Kułas M., 1993. Quantity methods of determination and investigation of fat. In: Investigation of food products quality. PWE Press, Warsaw.

Paul S. and Mittal G.S., 1996. Dynamics of fat/oil degradation during frying based on optical properties. J. Food Eng., 30, 389-403.

PN-A-86908, 2000. Oils and animal and plant fats. Refined plant oil. PKN Press, Warsaw, Poland.

PN-ISO 660, **1998.** Oils and animal and plant fats. Determination of acidic value and acidity. PKN Press, Warsaw, Poland.

PN-ISO 3960, **1996.** Oils and animal and plant fats. Determination of peroxide number. PKN Press, Warsaw, Poland.

Sikorski Z.E., 2000. Food Chemistry. Composition, Transformations and Properties of Food. WNT Press, Warsaw, Poland.

Staat F. and Vallet B., 1994. Vegetable oil methyl ester as a diesel substite. Chemistry and Industry, 7, 863-865.

Tys J., Piekarski W., Jackowska I., Kaczor A., Zając G., and Starobrat P., 2003. Technological and economical conditions for rape based biofuel production (in Polish). Acta Agrophysica, 99, 1-162.

Valdés A.F. and Garcia A.B., 2006. Study of the evolution of the physicochemical and structural characteristics of olive and sunflower oils after heating at frying temperatures. Food Chem., 98, 214-219.