Effect of Fried Dishes Assortment on Chosen Properties of Used Plant Oils as Raw Materials for Production of Diesel Fuel Substitute

Marek Szmigielksi, Barbara Maniak, Wiesław Piekarski and Grzegorz Zając
University of Life Sciences in Lublin
Poland

1. Introduction

Utilization of post-frying plant oils which are waste product of operation of, serving fried products, gastronomical points, for many years has been growing and complex problem of technological, ecological and economical nature. It must be noted that methods of solving this problem were subject of numerous research [Alcantara 2000; Buczek and Chwiłkowski 2005; Dzieniszewski 2007; Leung and Guo 2006]. Conception of utilization of post-frying plant oils as components for production of substitute of diesel fuel seems to be promising. However, it is necessary to investigate in detail properties of such oils, so that elaborated technologies of their utilization are optimal. Answer to question concerning influence of assortment of fried products on quality of post-frying oil, and its usefulness, when aspect of differences in utilization of particular batches of such oil, obtained after frying various food products, seems to be the most significant issue.

Most commonly used method of frying food in gastronomical points is deep frying. During this type of frying, processed food is submerged in frying medium and contacts oil or fat with most of its external surface. The main role of frying medium is keeping processed food in proper position to source of heat and transferring proper amount of heat energy into a fried product [Drozdowski, 2007; Ledóchowska and Hazuka, 2006]. Frying fat, which is a frying medium, and products subjected to culinary processing form a specific system in which partial penetration of these two compounds and two-way transfer of energy and weight take place. As a result of frying, product loses significant amount of water and, depending on its composition, some of its compounds e.g. food dyes, taste and flavour compounds and partially, transferred to frying fat, lipids. They are replaced with some amount of frying fat, which content in fried food, according to approximate data, may vary significantly and reach even 40% [Ledóchowska and Hazuka, 2006].

Water present in processed products and released during submersion frying has got diverse and multi directional influence on changes occurring in oil, among which is, causing partial increase of acid number (AN) of oil, fat hydrolysis. Moreover, transport of heat emitted with released water vapours favours decrease of temperature of fried food and partly inhibits oxidation transformations of fat by displacing oxygen in it [Ledóchowska and Hazuka, 2006].
Oxygen dissolved in frying fat together with water vapour are also significant factors of so-called thermooxidative transformations, which have not been fully explained yet. As a result of these transformations numerous substances, having complex and not fully determined structure, are formed. They are precursors of secondary transformations, products of which can be usually classified in one of two categories: volatile compounds (hydrocarbons, fatty acids and carboxylic compounds) and non-volatile (monomers, dimers, polymers and also some aldehydes and ketones, as well as fatty acids characterizing with changed melting point) [Drozdowski 2007, Paul and Mittal 1996, Blumenthal 1991, Choe and Min 2006, Clark and Serbia 1991, Hoffman 2004, Ledóchowska and Hazuka 2006].

Gastronomical fryers are usually containers having fairly high capacity, in which, next to the surface layer, which is environment determining properties of processed product, some volume of oil deposited near a bottom of a fryer can be distinguished. Bottom zone of a fryer, adjacent usually to the source of heat emission and having relatively low content of oxygen and water vapour, favours free radical or polymerization transformations of unsaturated fatty acids occurring in frying fat. The most common result of these transformations are numerous, having complex structure, non-polar thermal polymers. Macroscopic result of this type of reactions are increase of viscosity and darkening as well as increase of melting point of frying medium, what results in change of its state of aggregation. Products of these transformations are main components of dark brown deposits found on walls of a fryer, which can be a reason for many problems related to utilization of such oil [Hoffman 2004].

It should be noted that direction and intensity of frying fat transformations depends on numerous factors accompanying this process during frying of food products. In literature [Ledóchowska and Hazuka 2006] at least few groups of such factors are named. As the basic ones, conditions of carrying out the process (its duration, temperature and periodicity) and degree of unsaturation of fatty acids in triglycerides of fat, are mentioned. Among all factors affecting properties of frying medium many other, accompanying frying process, like oxygen availability and amount and composition of compounds released from food (e.g. pro and antioxidants and presence of water), play a significant role [Ledóchowska and Hazuka 2006].

2. Assessment of usability of post-frying edible oils as a raw material for production of diesel fuel substitute

2.1 Materials and methods
2.1.1 Preparation of samples for Investigation
In this research, comparison of influence of fried dishes assortment (potato chips and breadcrumbs coated fish fingers) on physicochemical properties and quality of post-frying plant oils to be utilized as raw materials for production of, used as a substitute of diesel fuel, fatty acids methyl esters, was conducted. Main focus of the research was on evaluation of effect of fried dishes assortment on quality of obtained post-frying oils (rapeseed, sunflower and soybean) with regard to their utilization as a substrate for production of engine biofuel. In model conditions of laboratory investigation, usability of post-frying waste oils as raw materials for production of fatty acids methyl esters was evaluated. Three most commonly used edible oils (rapeseed, sunflower and soybean) were used as material for this research. From total amount of each of raw oils, sample for laboratory analyses was taken. It was marked as “0” and was used as a reference sample. Remaining amount of each of oils was
divided into three batches and poured into separate containers. Batch no. 1 was prepared by means of cyclic, five-time heating without fried product. Particular cycle within this batch comprised of heating whole amount of oil to temperature of approximately 180°C, and than maintaining it in such temperature for 10 min. Next, oil was left to cool down in room temperature and than a sample, to be used for laboratory analyses, was taken. The sample was marked as "heating I - without fried product". After 24 hours all described above actions were repeated yielding sample marked as "heating II - without fried product". Whole process of heating, cooling and sampling was repeated, yielding samples marked as "heating without fried product" bearing following, respective to number of cycle, labels: III, IV and V.

Preparation of oil from batch no. 2 was differed from previously presented in only one way. After heating it to 180°C, in each of three investigated oils, potato chips, prepared of purchased raw potatoes and cut to the size and shape of frozen potato chips found in trade, were fried. After frying and separating chips, oil was cooled down to room temperature and than samples for research were taken. They were marked as "heating I - process of chips frying". Repeating whole process enabled obtaining samples marked following, respective to number of cycle, labels: III, IV and V.

Third part of oil (batch no. 3) was heated same way as batch no. 2 but in this case purchased breadcrumbs coated fish fingers were the fried product. After frying and separating breadcrumbs coated fish fingers, oil was cooled down to room temperature and than samples for research were taken. They were marked as "heating I - process of breadcrumbs coated fish fingers frying". Repeating whole process enabled obtaining samples marked following, respective to number of cycle, labels: III, IV and V.

2.2 Laboratory test
Oil samples obtained in conformity with chosen methodology were subjected to laboratory tests, which comprised of following analyses: determination of peroxide number (PN), acid number (AN) and composition of fatty acids. Determination of peroxide number (PN) in conformity with [ISO 3960] was based on titration of iodine released from potassium iodide by peroxides present in the sample, calculated per their weight unit. Results of analyses were expressed in millimoles of oxygen per weight unit of the sample.

Determination of acid number (AN) in conformity with [PN-ISO 660] was conducted by means of titration and evaluation of acidity of a sample, and expressed in numeric form in millilitres of 0,1M solution of sodium hydroxide, calculated per weight unit of analysed oil.

Determination of fatty acids composition was conducted by means of method based on utilization of gas chromatography [Krelowska – Kulas, 1993]. Sample of fat was subjected to alkaline hydrolysis in anhydrous environment with utilization of methanol solution of sodium hydroxide. As a result of this reaction, fatty acids of investigated oil were transformed into a mixture of sodium soaps, which than were subjected of reaction of esterification with anhydrous solution of hydrogen chloride in methanol, yielding mixture of fatty acids methyl esters.

Obtained methyl esters were separated in a chromatographic column and than their participation in a sum of fatty acids was determined [Krelowska – Kulas, 1993]. Chromatographic separation was conducted by means of gas chromatograph with nitrogen as carrier gas, packed column (2,5 m with stationary phase PEGA - polyethylene glycol adipate on carrier GAZ-ChROM-Q) and flame ionization detector.
2.3 Engine tests
Samples of soybean oil which remained after laboratory samples had been taken from each of three batches, differentiated by type of initial preparation (frying potato chips, frying breadcrumbs coated fish fingers and heating without fried product), were separately subjected to esterification with methanol. Fatty acids methyl esters were obtained by method analogous to the one used in investigation of fatty acids composition by means of gas chromatography. Fuel obtained this way was used in engine tests including main engine work parameters. Four mixtures were prepared, each containing 90% diesel fuel and 10% addition of fatty acids methyl esters obtained in research and marked as:

a. M1 - esters obtained from purchased fresh soybean oil,
b. M2 - esters obtained from soybean oil subjected to five-time cyclic heating, without addition of fried product,
c. M3 - esters obtained from soybean oil, previously used for five-time cyclic frying of potato chips,
d. M4 - esters obtained from soybean oil, previously used for five-time cyclic frying of breadcrumbs coated fish fingers.

Results of internal combustion engine running on diesel fuel (DF) were used as reference for determination of work parameters of engine powered with fuel blends. Above mentioned fuel mixtures, were used for powering 2CA90 diesel engine installed on dynamometric stand for purpose of conducting measurements of its energetic work parameters. Test bed comprised of following devices:

- internal combustion diesel engine 2CA90;
- dynamometric stand composed of eddy-current brake AMX210 and control-measurement system AMX201, AMX 211;
- fuel consumption measuring system;
- system measuring engine parameters: exhaust gasses temperature - tsp, engine oil temperature - tol, oil pressure -pol;
- system measuring state of environment: temperature of environment - tot, atmospheric pressure - pa, and air humidity - φ.

Measurements for each of investigated fuels were conducted and obtained results of energetic parameters were elaborated. Data yielded by measurements was used to draw external characteristics of the engine for rotational speed ranging from minimal to nominal. Carried out research included kinematic and dynamic parameters of the engine: torque - Mo, rotational speed - n, time in which set amount of investigated fuel was used - τ. Amount of fuel used for purpose of this characteristic was 50 g. Methodology of measurements and methods of measurements and results reduction of power and torque, were in conformity with norms: PN-88/S-02005, BN-79/1374-03.

3. Result of investigation
Raw, purchased plant oils characterised with typical properties, fulfilling requirements of recommended in Poland norm [PN - A - 86908] with regard to peroxide number (PN) and acid number (AN) (fig. 2 and 3).

Heating edible oils in conditions corresponding to frying potato chips, breadcrumbs coated fish fingers and heating without a product lead to significant changes of investigated oils properties. It caused mainly distinct changes of acid number (AN) and peroxide number (PN).
Differences in properties of oils subjected to cyclic heating without fried product and in which potato chips or breadcrumbs coated fish fingers were fried may result from course of temperature changes for various investigated batches (Fig. 1).

The highest temperature for each of investigated oils and in each of five heating cycles was observed in case of samples heated without fried products, in which temperature remained at 180°C. Changes of temperature of oil heated in the process of frying potato chips or breadcrumbs coated fish fingers had dynamic course, reaching the lowest value in approximately beginning of fifth minute. However, value of this minimum was depended on weight of fried product but main factor was fried product to frying medium weight ratio (fig. 1).

Conducted research show that heating plant oils caused noticeable increase of peroxide number (PN) value, when compared to samples not subjected to thermal processing. It
must be noted that diverse course and intensity of these changes were observed in case of samples heated without product, samples heated in process of potato chips and breadcrumbs coated fish fingers frying (Fig. 2).

Fig. 2. Peroxide number of rapeseed oil subjected to cyclic heating [mMO kg-1]/ data for oil heated in process of potato chips frying and heated without addition of product according to Szmigielski et al. 2008/

Typical course of peroxide number changes in relation to number of frying cycle was presented in Fig. 2. In case of each of five heating cycles, highest value of peroxide number in rapeseed and soybean oils was observed in samples heated without a product [Szmigielski et al. 2008]. It was characteristic, that in these samples peroxide number value increased fast until third or fourth cycle, after which decrease of its value was noted (Fig. 2). Most probable cause of such course of peroxide number changes, in relation to heating cycles, is formation of oxidation products, which partially evaporate from the environment of reaction in form of volatile products. An exception to the rule were analyses conducted for samples of soybean oil (first and second cycle of heating), in which temporarily highest value was observed in samples heated in process of breadcrumbs coated fish fingers frying [Szmigielski et al. 2011]. Most probably it results from influence of fat present in fried product on a final result of determination.
Samples of oil heated in the process of potato chips frying, characterised with lower values of peroxide number for each of five heating cycles, when compared to samples heated without the fried product. Stabilizing effect of potato chips, caused by sorption of oxidation products on their surface or partial absorption of frying fat, is most commonly mentioned probable cause of such course of PN changes in these samples [Maniak et al. 2009, Szmigielski et al. 2008, 2009, 2011]. It should be noted (Fig. 1) that PN level in samples of rapeseed and soybean oil heated in process of potato chips frying [Szmigielski et al. 2008], had similar course, stabilizing respectively at approx. 2 mMo/100g and approx. 1.5 mMo/100g [Szmigielski et al. 2011] (with exemption of null samples and first cycle of soybean oil heating). Results of investigation of soybean and rapeseed oil samples heated without fried product differed significantly - reaching almost two times higher value of peroxide number (PN) than respective samples heated in process of potato chips frying. As opposed to this research, heating sunflower oil in process of potato chips frying caused only slight decrease of its peroxide number (PN) when compared to samples heated without fried product [Maniak et al. 2009].

Typical course of acid number (AN) changes of heated oil samples in relation to number of frying cycles was presented in Fig. 3. Acid number of heated oil samples was higher than in raw oil, however, heating in process of potato chips frying caused stabilization of acid number value (AN) at similar level (0,02 mgKOH/g) regardless of number of oil heating cycles, while heating without the product caused systematic increase of AN. Very similar course of acid number changes of investigated post-frying oils was also observed in analogous research on rapeseed oil [Szmigielski et al. 2008] and sunflower oil samples [Maniak et al. 2009]. It is believed, that the most probable cause of observed changes of acid number of these samples is sorption of oxidation products on surface of, subjected to culinary processing, potato chips or partial absorption of oil surrounding the product into its deeper, more distant from surface of investigated raw product layers.

Acid number (AN) of plant oils (rapeseed and soybean) heated in the process of frying breadcrumbs coated fish fingers was increasing systematically. It should be noted that AN for first two cycles of heating remained at level similar or lower than AN determined in respective samples heated in the process of potato chips frying. However, starting from the third heating cycle AN exceeded this value and was systematically increasing with each of heating cycles, reaching values lower than in respective samples of soybean oil heated without fried product (fig. 3). It is believed that two opposing processes were the most probable cause of above described course of changes of acid number (AN) in samples of oils heated in process of breadcrumbs coated fish fingers frying. Increase of AN value should probably be explained with oxidation of fatty acids and hydrolytic effect of water vapour, released from product as a result of frying, while reduction of its level occurred as an effect of sorption of oxidation products on surface of fried product [Szmigielski et al. 2009; 2011]. Five-time cyclic heating of plant oils caused significant changes in composition of fatty acids, which can be simply characterised as significant decrease of fatty acids content. It concerns mainly unsaturated fatty acids, and significant increase of oxidation products content, what can be easily observed on example of soybean oil (fig. 4-6). Similar course of fatty acids composition changes of investigated post-frying oils was also observed in research of, subjected to cyclic heating, samples of rapeseed oil [Szmigielski et al. 2008;2009] and sunflower oil [Maniak et al. 2009]. Five-time cyclic frying of breadcrumbs coated fish fingers or potato chips caused partial stabilization of fatty acids composition, what can be noted in case of two, dominating in soybean, fatty acids i.e. oleic and linolic. Their content in typical raw soybean oil often exceeds 75% (fig. 3-5), [Staat and Vallet 1994, Tys et al. 2003].
Heating this oil only slightly changed proportion of oleic to linolic acid, for in raw oil, on one particle of oleic acid approx. two particles of linolic acid are found. After process of heating, this rate is approx. 1.5 - from 1.4 for sample heated without fried product to 1.50 for sample heated in the process of frying potato chips, and up to 1.63 when sample of oil heated in the process of frying breadcrumbs coated fish fingers is investigated.

Similar effect, when ratio of unsaturated fatty acids (oleic and linolic) is taken into consideration, was also observed in research of sunflower oil used as frying fat in cyclic frying of potato chips.

Fresh sunflower oil usually contains over 80% of these fatty acids, while, statistically on one particle of oleic acid 2.47 particles of linolic acids are found. After five-time cyclic heating in process of potato chips frying this proportion remains unchanged, while it changes only in case of oil heated without fried product [Maniak et al. 2009].

In fresh rapeseed oil, proportion of linolic acid to oleic acid is 1 : 2.72. Five-time cyclic heating in process of potato chips frying caused significant change of this proportion to 1 : 2.37, while, for example, effect of disturbance of this fatty acids ratio occurring during similar cycle of heating without fried product reached 1:3.77 [Szmigielski et al. 2008]. The same processes of heating caused also slight changes of saturated fatty acids ratio. In fresh soybean oil, on one particle of stearic acid 2.66 particles of palmitic acid are found, while after five cycles of heating this ratio was from 1 : 2.1 in oil heated without product (Fig. 4), 1 : 2.31 in oil subjected to heating in process of potato chips frying (Fig. 6) to 1 : 2.38 in oil subjected to heating in process of breadcrumbs coated fish fingers frying (Fig. 5).

Fig. 3. Acid number of rapeseed oil subjected to cyclic heating [mgKOH g⁻¹]/ data for oil heated in process of potato chips frying and heated without addition of product according to Szmigielski et al. 2008/
Fig. 4. The composition of fatty acids of soybean oil treated five-time cyclic heating, heating without fried product /presented data based on authors own research [Szmigielski et al. 2011]/
Fig. 5. The composition of fatty acids of soybean oil treated five-time cyclic heating, heating in process of breadcrumbs coated fish fingers frying /presented data based on authors own research [Szmigielski et al. 2011]/
Effect of Fried Dishes Assortment on Chosen Properties of Used Plant Oils as Raw Materials for Production of Diesel Fuel Substitute

Fig. 6. The composition of fatty acids of soybean oil treated five-time cyclic heating heating in process of potato chips frying /presented data based on authors own research [Szmigielski et al. 2011]/
Similar, slight fluctuations of stearic and palmitic acids ratio were noted after five-time cyclic heating of rapeseed oil, and ranged from 1 : 2.97 in fresh oil, to 1 : 3.03 after heating in process of cyclic potato chips frying and 1 : 2.94 after cyclic heating without fried product [Szmigielski et al. 2008].

It should be noted that similar cyclic heating of sunflower oil did not cause change of ratio of two main saturated fatty acids present in investigated oil e.g. stearic acid and palmitic acid. The ratio was 1 : 1.69. Both in fresh sunflower oil and in oil after five-time cyclic heating without fried product or heated in process of potato chips frying, this ratio did not change [Maniak et al. 2009].

Presented in graphs 7-10 research data, obtained during engine tests, in which mixtures of diesel fuel containing 10% of fatty acids methyl esters were utilised, indicate on similar character of changes of investigated parameters of 2CA90 engine powered with methyl esters obtained from purchased raw soybean oil and post-frying oils obtained after five-time cyclic heating without fried product as well as five-time cyclic frying of potato chips or breadcrumbs coated fish fingers. Mixtures containing 10% addition of esters have similar influence on changes of power and torque of investigated engine in relation to its rotational speed (Fig. 7 and 8).

Curves of specific and hourly fuel consumption for investigated fuel mixtures, containing 10% addition of fatty acids methyl esters, characterised with higher values of energetic parameters, when compared to diesel fuel, for each of five investigated rotational speeds. It should be noted that they characterize with identical nature and high similarity of their course, what suggests insignificance of differences between them. Analogous results of research were obtained by Szmigielski et al. [2009], who, in similar conditions, investigated rapeseed oil samples.

4. Conclusion

1. Model, cyclic heating of plant oils, and especially three first cycles, contribute to significant changes in composition of their fatty acids. Significant changes of peroxide number (PN) and acid number (AN) of investigated oils were noted. Content of unsaturated fatty acids decreases, while increase of oxidation products is observed.
2. Heating plant oils in process of frying products like breadcrumbs coated fish fingers or potato chips affects stabilization of amount of peroxide products present in post-frying oil, what leads to decrease of peroxide number (PN) of such oil in comparison to process of heating without fried products.
3. Acid number (AN) of post-frying oils obtained after frying potato chips stabilized, while frying breadcrumbs coated fish fingers and heating oil without fried product contributed to gradual increase of AN.
4. Frying breadcrumbs coated fish fingers and potato chips favours stabilisation of proportion of fatty acids in investigated post-frying oils, and the proportion is similar to one noted in case of purchased raw oils.
5. Change of properties of post-frying plant oils occurring during stage of chemical conversion to fatty acids methyl esters, contributes to unification of properties of biofuels prepared on base of various batches of post-frying oils and favours utilization of post-frying oils which proved as suitable for production of biofuel as fresh vegetable oils.
6. Unidentified oxidation products undergo similar transformations in the process of fatty acids methyl esters formation, and are not a significant obstacle in correct operation of diesel engines powered with such biofuel.
7. Results of research confirmed usability of post-frying plant oils as a raw material for production of diesel fuel biocomponent.

8. It is currently necessary to elaborate efficient ways of recovery of post-frying fats from points of small gastronomy, and technology of their purification and utilization as components of fuel for diesel engines.

Fig. 7. Changes of the course of engine power 2CA90 powered by diesel fuel (ON) and mixtures containing 90% diesel fuel and 10% methyl esters of fatty acids and diesel fuel: M1 - esters obtained from purchased fresh soybean oil, M2 - esters obtained from soybean oil without addition of fried product, M3 - esters obtained from soybean oil frying of potato chips, M4 - esters obtained from soybean oil frying of breadcrumbs coated fish fingers. /presented data based on authors own research /[Szmigielski et al. 2011]/
Fig. 8. Changes of the course of engine torque 2CA90 powered by diesel fuel (ON) and mixtures containing 90% diesel fuel and 10% methyl esters of fatty acids and diesel fuel: M1 - esters obtained from purchased fresh soybean oil, M2 - esters obtained from soybean oil without addition of fried product, M3 - esters obtained from soybean oil frying of potato chips, M4 - esters obtained from soybean oil frying of breadcrumbs coated fish fingers. /presented data based on authors own research /[Szmigielski et al. 2011]/
Fig. 9. Changes of the course of unitary fuel consumption engine 2CA90 powered by diesel fuel (ON) and mixtures containing 90% diesel fuel and 10% methyl esters of fatty acids and diesel fuel: M1 - esters obtained from purchased fresh soybean oil, M2 - esters obtained from soybean oil without addition of fried product, M3 - esters obtained from soybean oil frying of potato chips, M4 - esters obtained from soybean oil frying of breadcrumbs coated fish fingers. /presented data based on authors own research /[Szmigielski et al. 22011]/
Fig. 10. Changes of the course of hourly fuel consumption engine 2CA90 powered by diesel fuel (ON) and mixtures containing 90% diesel fuel and 10% methyl esters of fatty acids and diesel fuel: M1 - esters obtained from purchased fresh soybean oil, M2 - esters obtained from soybean oil without addition of fried product, M3 - esters obtained from soybean oil frying of potato chips, M4 - esters obtained from soybean oil frying of breadcrumbs coated fish fingers. /presented data based on authors own research /[Szmigielski et al. 2011]/

5. References


Effect of Fried Dishes Assortment on Chosen Properties of Used Plant Oils as Raw Materials for Production of Diesel Fuel Substitute


Polish Norm PN-ISO 660, Oleje i tłuszcze roślinne oraz zwierzęce – Oznaczanie liczby kwasowej i kwasowości, PKN 1998.

Polish Norm PN-ISO 3960, Oleje i tłuszcze roślinne oraz zwierzęce – Oznaczanie liczby nadtlenkowej, PKN 1996.


Szmigielski M., Piekarski W., Maniak B., Zając G., Masłowski A.& Biernacka B. (2011) Influence of fried meals assortment on selected postfrying soya-bean oil features as components to produce diesel biocomponents International Agrophysics (in review), ISSN 0236-8722.
This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following: