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IMPROVEMENT OF QUALITY OF USED FRYING OIL BY MEANS OF ACTIVE CARBONS

Summary: The results of studies on application of a mixture of active carbons of different surface properties in the process of purifying used frying oil are presented. The applied active carbons were prepared by heating commercial active carbon to temperature of 1000°C (ARW) and by oxidation with hydrogen peroxide (ARP2). Used frying rapeseed oil, for deep-frying of foodstuffs, was subjected to the adsorptive treatment. The frying medium was refined oil that allowed long-lasting deep-frying (Pan Max) owing to retardation of the oxidation process. The treatment with a mixture of active carbons caused a reduction in the amount of colour bodies, the products of primary and secondary oxidation, and, in addition, hydrolysis products of fatty acids and polar compounds.

Keywords: used frying oils, oil degradation products, active carbons.

1. Introduction

Fast-food restaurants use mineral adsorbents to extend the useful life of frying oil to increase frying effectiveness and economise of the process. These substances may extend the oils' life by up to 9 days [Cooke 2006, 2007; Buczek 2011]. This is due to the polar nature of these adsorbents, owing to which they retain polar compounds formed as a result of frying food. The technologies used for extending the life of frying oils in restaurant chains include the application of mineral adsorbents along with an oil change at the end of each processing day. Due to this treatment it has been possible to maintain an appropriate quality for the frying oil over a longer period. This activity may certainly be justified both economically and ecologically. On the one hand, it contributes to a rise in restaurant owners' profits, while on the other, it reduces the amounts of waste oil produced in the restaurant.

The result of long-lasting deep fat frying is the formation of low- and high-molecular organic structures. The chemical compounds formed, like free fatty acids, hydroxides, polymers and other products of primary and secondary oxidation, affect the quality of the frying oil used, and consequently, may cause health problems in consumers of the products prepared with these fats. Undesirable oil soluble

substances, firstly, give rise to the acceleration of fat degradation; next, they destructively affect the quality and nutritive value of the medium, which may be confirmed by the deterioration, above all, of the flavour, consistency and colour of the frying oil. Such material, from a consumer's point of view, should not be used any more. This is entirely clear; however, used frying-oil still contains many components that are still usable. These are the triacylglycerols which, after separation from the components that cause the oil degradation, may still be employed as a frying medium and be providers of polyene acids. Because of this, in order to extend the useful life of the oil, adsorption treatment should be applied that will remove the unfavourable compounds causing oil degradation.

It seems that active carbons, due to their sorptive properties, may meet the requirements set for treating used frying oil. Regrettably, microporous carbon adsorbents do not show appropriate surface characteristics. They are generally non-polar adsorbents. Because of this, to make active carbons useful for the adsorption of polar compounds, they should be subjected to chemical modification.

The aim of this process would be to introduce additional surface groups or rearrange them, leading to a change in the surface character to make it polar. A number of methods for the modification of active carbons to make them suitable for used frying oil treatment have already been studied, *inter alia*, liquid phase oxidation with nitric acid, hydrogen peroxide, as well as heat treatment in a nitrogen atmosphere [Buczek, Chwiałkowski 2008, Buczek 2010, *Sposób regeneracji…* 2012, Jankowska i in. 1985].

This paper presents the results of studies on the application of a mixture of heat treated and oxidised active carbons for the treatment of used frying oil. The changes in the physical and chemical properties, quality parameters, and fatty acid content after using the frying oil and after adsorption treatment were analysed.

The aim of the study was to determine the effectiveness of the adsorption of frying-oil degradation products by means of a mixture of active carbons with different surface properties.

2. Materials and methods

2.1. Materials

Fresh frying oil PM with the trade name "Pan Max" – a refined liquid fat with natural sediment, manufactured from rapeseed oil by ZT "Kruszwica" S.A., Poland.

Used frying oil PMZ – frying oil PM used for frying potato chips produced by RS Markenvertrieb GmbH & Co. KG Aldrup, Germany, ca. 25 kg potato chips were fried at a temperature of 170÷175 °C in a household fryer over a 4-day period.

Active carbon AR made from charcoal by steam activation, manufactured by ZEW Racibórz (at present Elbar – Katowice Sp. z o.o., Carbon Division in Racibórz).

Active carbon ARW obtained from AR active carbon by treatment in a 99.9% nitrogen atmosphere at a temperature of 1000 °C.

Active carbon ARP2 obtained from AR active carbon by liquid phase oxidation with 30% solution of hydrogen peroxide.

2.2. Analysis of surface properties and pore structure of active carbons

The pore structure of active carbons was analysed based on the low-temperature nitrogen adsorption isotherm that was determined using a volumetric method at the temperature of 77.5 K in the range of relative pressures p/p_0 = 0.00001÷0.999.

From the data obtained, parameters characterising the microporous structure were determined: micropore volume (W_0) and characteristic adsorption energy (E_0) according to the Dubinin-Radushkevich equation [Dubinin 1987]. The mesopore surface area (S_{mez}) was calculated with a Dollimore-Heal method [Dollimore-Heal 1964]. The specific surface area (S_{BET}) was determined from the Brunauer-Emmett--Teller (BET) equation [Bansal, Goyal 2009].

Table 1 presents the results of the analysis of the micro- and mesoporous structure of the carbons investigated.

**Table 1.** Parameters of porous structure of AR, ARW and ARP2 active carbons

Parameter	Symbol	Unit	AR	ARW	APR2
Micropore volume	W_0	cm³/g	0.423	0.395	0.372
Characteristic adsorption energy	E_0	kJ/mol	18.5	21.5	21.1
Mesopore surface area	S_{mez}	M²/g	207	165	180
Specific surface area	S_{BET}	M²/g	980	945	915

Source: author's work.

The AR active carbon modification by heat treatment in a nitrogen atmosphere and oxidation with hydrogen peroxide yielded adsorbents of reduced micropore volume, and smaller mesopore and specific surface areas. In the case of ARW carbon, the W_0 parameter was reduced by almost 7%; the mesopore surface area by more than 20%; and the BET surface area by nearly 4%. The second active carbon is characterised by a micropore volume lower by over 12% and a mesopore surface area lower by nearly 7%. A positive change was an increase in the characteristic adsorption energy for both adsorbents. The value of E_0 for the carbon heat treated in the nitrogen atmosphere rose by over 16%, and for the carbon oxidised by hydrogen peroxide by over 14%.

In order to determine the type of oxygen-containing functional groups occurring at the surface of adsorbents, carbon samples were subjected to the studies using the thermogravimetric method combined with an analysis of the evolving gases. The analyses were performed at a heating rate of 10 °C/min, from a temperature of 25 to

1000 °C, at a He flow rate of 6 dm³/h. An SDT 2960 TA INSTRUMENTS thermobalance with 10^{-7} g sensitivity coupled with a QMS 300 BALZERS quadrupole mass spectrometer of 1 u sensitivity was used.
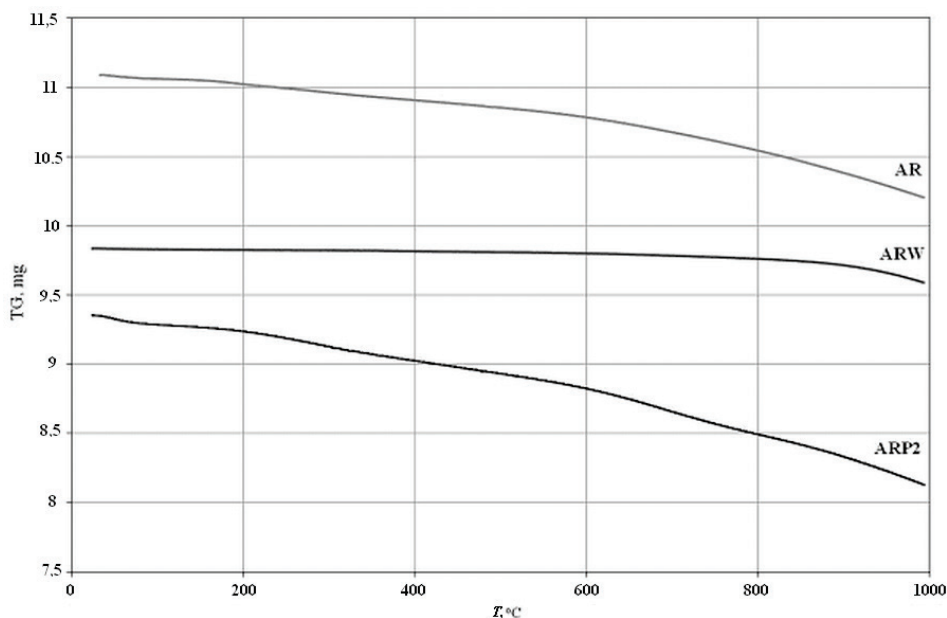
Fig. 1. TG curve for AR, ARW and ARP2 active carbons

Source: author's work.

Mass losses were calculated for the individual active carbons from the TG curves presented in Fig. 1. The mass changes were calculated in the temperature ranges: 25÷180 °C, 180÷700 °C and 700÷1000 °C. These ranges are interesting as they define the evolution of various gas products. In the first temperature range, water, chiefly hygroscopic, evaporates. In the second range, the evolution of CO_2, formed as a result of acid group decomposition, comes to an end. The third range corresponds to the end of CO evolution being the result of the destruction of basic groups [Biniak i in. 1997] Table 2 presents the calculation results.

Comparing the mass losses in the individual temperature ranges (Table 2), as a result of the high temperature treatment of the AR active carbon, almost all acidic groups were removed from its surface (reduction by 87%), and the number of basic surface groups decreased by over half. In the case of the oxidation of the starting active carbon using hydrogen peroxide, the content of both the acidic and basic functional groups increased. The rise in the amount of groups of acidic character was nearly 100% and in those of a basic character by ca. 40%. The surface of ARP2 active carbon was covered with functional groups of both characters to practically the same degree.

Table 2. Mass losses for active carbons determined from TG curves

Active carbon	Mass loss in the temperature range, %		
	25÷180 °C	180÷700 °C	700÷1000 °C
AR	0.46	3.27	4.40
ARW	0.11	0.43	1.99
ARP2	1.09	6.42	6.10

Source: author's work.

In order to determine the type of individual acidic functional groups on the surface of active carbons, Boehm's method was used [Boehm 2002]. Samples of active carbons were treated with the following solutions: 0.1 M $NaHCO_3$, 0.5 M $NaCO_3$ and 0.1 M NaOH; next, the mixtures were shaken for 24 h. The specified reagents neutralise in the aqueous environment acidic groups of a pK value characteristic of them. Sodium hydrogen carbonate neutralises carboxylic groups, sodium carbonate, carboxylic and lactone groups, and sodium hydroxide, carboxylic, lactone and hydroxyl groups. The excess of the reagent applied was back titrated with 0.1 M HCl to methyl orange until the solution changed colour. Table 3 presents the results of the analyses.

Table 3. Results of the determination of oxygen-containing acidic groups

Active carbon	Surface acidic group contents, μmol/g		
	Highly acidic carboxylic groups	Lactone groups of medium acidity	Weakly acidic hydroxylic groups
AR	50.1	0.4	789.3
ARW	0.0	235.1	55.2
ARP2	439.8	112.2	77.9

Source: author's work.

The analysis of surface acidic group content demonstrated that the heat treatment of AR active carbon leads to total degradation of carboxylic groups and the conversion of a large number of hydroxyl groups into lactone groups. The fraction of the latter was 81% on the surface of ARW active carbon. Moreover, ARW active carbon contained a small number of hydroxylic groups. As a result of the oxidation of commercial AR active carbon with hydrogen peroxide, a significant fraction of hydroxyl groups was oxidised to carboxylic groups. The content of hydroxylic groups decreased from 94 to 12%, whereas the carboxylic group content rose from 6 to 70%. On the surface of the active carbon oxidised by hydrogen peroxide, lactone groups also appeared. They constituted 18% of the surface acidic groups in the AERP2 active carbon.

2.3. Treatment of the used oil

The used frying oil PMZ was subjected to treatment by means of an equivalent mass mixture of ARW and ARP2 active carbons. The active carbons were selected based on previous investigations, in which they were used separately [Buczek, Chwiał-kowski 2008; Buczek 2010]. A sample of oil was mixed with the adsorbents in a 1:20 (m/m) ratio. The suspension was heated and stirred by means of a magnetic stirrer for 30 min, while the temperature was kept at 70÷80 °C. Following this stage, the active carbon was separated by filtration of the warm suspension (60 °C) in a pressure filter in a nitrogen atmosphere. As a result of the treatment and filtration, the oil denoted PMO20 was obtained.

2.4. Testing methods of the frying medium

The aim of the used frying oil treatment was to remove the decomposition products formed upon frying potato chips and to assess the effectiveness and effects of the used mixture of adsorbents. To evaluate the changes in the properties of the fresh oil, used for frying and after treatment, the following physicochemical and quality parameters were used:
– colour, measurement accuracy ±0.001 [PN-A-86934],
– iodine value, IV ± 2.0 for IV Î < 50, 100 > [PN-ISO 6320:1995],
– acid value, AV ±3% [PN-ISO 660:1998],
– peroxide value, PV ±0.2 meq active O_2/kg [PN-ISO 3960:1996],
– anisidine value, AnV ±0.2 [PN-EN-ISO 6885],
– total oxidation index of fat, Totox [PN-93-A-86926],
– polar compound content, PC (oil quality tester OIL METER FOM 200, measurement accuracy: ±2%),
– fatty acid content was determined gas chromatographically [PN-EN ISO 5508:1996] in the form of methyl esters [PN-ISO 5509:1996].

   Table 4 gives the physicochemical and quality parameters at various treatment stages, Table 5 presents fatty acid contents, and Table 6 shows the contents of individual groups of fatty acids (SFA – saturated fatty acids, MUFA – monounsaturated fatty acids, PUFA – polyunsaturated fatty acids, UFA – unsaturated fatty acids).

Table 4. Physicochemical properties and quality parameters of the analysed oils

Oil	Colour	IV gI$_2$/100 g	AV MgKOH/g	PV mequiv O$_2$/kg	AnV	Totox	PC %
PM	3.3	86.60	0.083	0.58	1.28	2.43	0.2
PMZ	106.3	67.66	0.829	8.42	54.68	71.53	21.8
PMO20	62.3	82.60	0.724	5.77	44.90	56.43	18.4

Source: author's work.

Table 5. Main fatty acids content of oils determined by GC, wt. %

Fatty acids, %	PM	PMZ	PMO20
$C_{14:0}$	0.17±0.01	0.53+0.03	0.64±0.03
$C_{16:0}$	8.24±0.25	22.57±0.68	21.97±0.66
$C_{16:1\ (cis-9)}$	0.23±0.01	0.27±0.01	0.19±0.01
$C_{18:0}$	3.24±0.10	4.04±0.12	4.04±0.12
$C_{18:1\ (cis-9)}$	73.66±2.21	61.13±1.83	62.00±1.86
$C_{18:2\ (trans)}$	1.65±0.05	0.71±0.02	0.69±0.02
$C_{18:2\ (trans-9,12)}$	1.69±0.05	0.96±0.03	0.87±0.03
$C_{18:2\ (cis-9,12)}$	5.62±0.17	5.86±0.18	5.82±0.17
$C_{18:3\ (cis-9,12,15)}$	0.39±0.01	0.18+0.01	0.19±0.01

Source: author's work

Table 6. Total SFA, MUFA and PUFA contents, UFA/SFA

Fatty acids, %	PM	PMZ	PMO
SFA	14.19	28.93	28.38
MUFA	76.47	62.98	63.76
PUFA	9.34	7.72	7.57
UFA	85.81	70.70	71.32
UFA/SFA	6.05	2.44	2.51

Source: author's work

3. Results and discussion

Frying such a large amount of potato chips (25 kg) resulted in dramatic changes in the frying oil. The acid value increased tenfold, peroxide value almost fifteen-fold and anisidine value over 42 times. Another unfavourable phenomenon was the increase in polar compound content by over 100 times and colour value over 30 times. The amount of unsaturated substances expressed as the iodine value was reduced by almost 22% as a result of heat treatment (cf. Table 4).

The effect of frying was a twofold increase in the amount of saturated fatty acids (SFA) and a decrease in the total amount of unsaturated fatty acids (UFA) by about 15 units. The smallest changes were observed for polyene unsaturated fatty acids (PUFA), for which it was ca. 2 wt. %. The ratio of the amount of unsaturated to saturated fatty acids, which was equal to 6, decreased by about 60%, reaching the value of 2.44 (cf. Table 6).

In the case of saturated fatty acids, the evident changes concern myristic ($C_{14:0}$), palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acids. In the group of these acids, the increase was, respectively, over twice, by about 14 units, which corresponds to a rise of over 170%, and in the case of stearic acid, by about 25% with respect to their content in the starting fresh oil. In the group of monounsaturated acids, the amount of *cis*-9

isomer of oleopalmitic acid ($C_{16:1,\ cis\text{-}9}$) decreased by about 12 units, which corresponded to a change of 17%. The total amount of trans isomers of linolic acid ($C_{18:2\ trans} + C_{18:2\ trans\text{-}9,12}$) was lowered by about 50%. Frying the potato chips also caused a reduction in the amount of *cis*-9,12,15 isomer of linolenic acid by over half (cf. Table 5). Based on the obtained quality index values, it can be stated that the rapeseed frying oil had been exploited to a very high degree.

Adsorption purification with a mixture of active carbons of different surface properties (ARW and ARP2) gave rise to an improvement in the quality and physicochemical parameters. The adsorption process worked best for the removal of colour bodies, products of primary (PV) and secondary (AnV) oxidation, and polar compounds content (PC).

The Colour Value decreased by over 41%, Peroxide Value by about 31%, Anisidine Value by about 18%, and the total amount of polar compounds by over 15% compared to the respective values for the used frying oil PMZ. Moreover, the hydrolysis products of fatty acid content (AV) decreased by over 12% as a result of contact with the mixture of adsorbents. Owing to the changes in the amounts of primary and secondary oxidation products, the value of the general total oxidation index, Totox, changed by over 21%. It is particularly puzzling that the Iodine Value rose by over 22% (cf. Table 4). Probably as a result of catalytic processes which take place on the surface [Giugato i in. 2004] highly acidic active carbon.

Contact between the mixture of active carbons and the used frying oil did not significantly change fatty acid content. It is therefore difficult to compare the results obtained. These have been shown only to demonstrate the character of the adsorbent activity.

Adsorption purification gave rise to a reduction in the amount of saturated acids (SFA) and polyunsaturated components (PUFA) by about 2%. Monounsaturated fatty acid content increased by about 1%. The ratio of unsaturated to saturated fatty acids rose by nearly 3% (cf. Table 6). As for the detailed analysis of the fatty acid profile, the following should be mentioned: a rise in myristic acid content by 21% and a fall in the amount of *cis*-9-oleopalmitic acid by ca. 32%, as well as a reduction in the *trans* isomer of linolic acid content by almost 7%. Changes in the amounts of other main components were significantly below 5% (cf. Table 5).

4. Conclusions

Based on the research conducted, the following may be concluded:

1. Adsorption purification of used frying oil using a mixture of active carbons of different surface properties (ARW and ARP2) causes advantageous changes with respect to the oil's physicochemical and quality parameters, owing to which the oil's lifetime is effectively extended.

2. Adsorbents used in the treatment caused an effective reduction, by over 40%, in the colour body content and in the primary oxidation product amount by over 30%. Their use also caused a drop in the free fatty acid, secondary oxidation product, and polar compound content and a rise in the fraction of unsaturated compounds.

3. Treating the used frying oil using a mixture of the active carbons analysed (ARW and ARP2) only affects the fatty acid composition insignificantly.

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POPRAWA JAKOŚCI ZUŻYTEGO OLEJU SMAŻALNICZEGO ZA POMOCĄ WĘGLI AKTYWNYCH

Streszczenie: W pracy przedstawiono wyniki badań nad wykorzystaniem węgli aktywnych o różnych właściwościach powierzchniowych do oczyszczania zużytego medium smażalniczego. Stosowane węgle aktywne przygotowano przez wygrzewanie handlowego węgla aktywnego w temperaturze 1000 °C w atmosferze azotu (ARW) oraz przez utlenianie nadtlenkiem wodoru (ARP2). Oczyszczaniu poddano fryturę, wyprodukowaną z oleju rzepakowego, przeznaczoną do smażenia w głębokim tłuszczu produktów żywnościowych. Medium smażalniczym był rafinowany olej rzepakowy z naturalnym osadem, pozwalający na długotrwałe smażenie dzięki opóźnieniu procesu oksydacji. Oczyszczanie oleju po smażeniu frytek za pomocą mieszaniny węgla ARW i ARP2 efektywnie poprawiło jego jakość. Traktowanie mieszaniną adsorbentów spowodowało obniżenie ilości substancji barwnych, produktów pierwotnego i wtórnego utleniania, także produktów hydrolizy kwasów tłuszczowych i związków polarnych. W wyniku oczyszczania wzrosła również ilość substancji o charakterze nienasyconym.

Słowa kluczowe: używana frytura, produkty rozpadu oleju, węgle aktywne.