Purification of the used palm oil by adsorption

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The components of fresh vegetable oils are mainly non-polar. During frying of food, complex and multistage reactions occur in the oil, which produce various polar compounds. Active carbons are characterized by small contents of polar functional groups, which are responsible for adsorbing such polar compounds. Effective purification of the used frying oils must involve the removal of the polar substances. To improve the quality of the used palm oil, an active carbon oxidized by a hydrogen peroxide treatment was used. Such a carbonaceous adsorbent improves the quality of the oil used for frying food by purifying it from colour substances, lipid hydrolysis products, oxidation products and total polar compounds.

Keywords: purification of used frying oil, active carbon, adsorption.

INTRODUCTION

Frying in deep fat is one of the most popular methods of preparing food, because of specific sensory values such as the flavour and the smell of the fried food, as well as an easy and fast way of preparing basic meals. Usually, in order to serve French chips or some other snacks, households and commercial food processors use vegetable fats. Oils are sources of polyenic fatty acids, which are indispensable for the normal functioning of the human body. As vegetable oils are unstable products and, when used for frying food undergo various transformations easily, one should not often consume fried food, especially fried in the oil of low quality.

Compounds of fresh vegetable oil, in the presence of oxygen, light, moisture and also at higher temperatures, undergo a complex series of changes and reactions during frying. Changes in the oils lead to the deterioration of their smell and taste, and to the formation of various chemical compounds (free radicals, peroxides, polymerisation and hydrolysis products, low molecular compounds and conjugated dienes, the products of the decomposition of hydroperoxides, hydrolysis of triglycerides and polymerisation). They are often very harmful and cause a decrease in the quality and the structural properties of the oil, and also accelerate its breakdown. The substances, which then form have a more or less chemical polar character.

In order to stop the progressive deterioration, some operation is required. The simplest solution is a frequent exchange of the used frying oil for a new one, however this generates the economical and ecological problems.

The purification of the used frying oils with adsorbents may improve the quality of the oils as well as of the fried food. The recovery of the used oil could be achieved by removing the undesirable oxidised, polar, colour substances and polymers. Various adsorbents could be used: mineral[1,2] and carbonaceous[3 – 5]. The first group is more popular because of their polar surface character, which helps to adsorb polar compounds most effectively. Unfortunately, mineral adsorbents such as magnesium silicate cause utilization problems.

Active carbon adsorption might be an alternative purification procedure, but some additional processing is required. Active carbons have large surface areas and extended microporous structures, but are characterised by small contents of polar groups. The purification of the used frying oils needs to remove the products of their degradation and such systems do not succeed. The oxidation of active carbon leads to the modification of its surface to a more polar one. Concentrated mineral acids, e.g. sulphuric and nitric, and hydrogen peroxide[6,7] are usually used as oxidation agents in the liquid phase. An oxidation process causes a change in the nature of the surface as well as in the texture of the carbonaceous adsorbent.

The objective of this study was the removal of degradation and oxidation products from palm oil used for frying potato chips, by its adsorption on the oxidised commercially produced active carbon.

EXPERIMENTAL PROCEDURES

Materials

OP – fresh hydrogenated palm oil – Master Frit – Unigra'Spa, Italy.

OPR – hydrogenated palm oil – used for frying French chips in the fryer (20 dm^3) at the temperature of $180 \div 186°C$ for 3 days, about 100 kg chips were prepared,

ARP – oxidised active carbon – obtained from active carbon AR, produced by ZEW Racibórz – (currently Carbon Racibórz Sp. z o.o. Poland) by the hydrogen peroxide oxidation.

Oxidation of active carbon

Dry active carbon AR was treated with a 30% solution of hydrogen peroxide. For 25g of active carbon 552 cm^3 of solution was provided, and then the mixture was mixed for 2 hours. After the oxidation process, the suspension was decanted and the adsorbent was washed in the distilled water to achieve the pH level of about 4. The so-obtained carbon ARP was next dried at the temperature of 120°C for 5 hours.

Analysis of the porous structure of active carbon

Porous structure was analysed on the basis of low-temperature nitrogen adsorption at the temperature of 77.5K in the relative pressure range $p/p_0 = 0.0001 – 0.999$. The parameters of the microporous structure: micropores volume (W_0) and the characteristic adsorption energy (E_0) according to the Dubinin-Radushkevich equation[8] were derived from these data. The mesopores surface area (S_{mes}) was calculated from the Dollimore-Heal[9] and the surface area (S_{BET}) from the Brunauer-Emmett-Teller equations[10] The Dubinin-Sierpinsky equation was used[11] in evaluating from the water sorption isotherm (a_0) – the number of adsorption centres among

Table 1. The properties and parameters of the porous structure of active carbons

Parameter	Symbol	Unit	AR	ARP
Micropores volume	W_0	cm^3/g	0.423	0.372
Characteristic adsorption energy	E_0	kJ/mol	18.5	21.1
Mesopores surface area	S_{me}	m^2/g	207	180
Surface area	S_{BET}	m^2/g	980	915
Number of surface group	a_0	mmol/g	1.54	5.32

surface groups. The results of the calculations are presented in Table 1.

As a result of active carbon's oxidation, the carbonaceous material with a high value of characteristic adsorption energy (E_0) and more surface functional groups (a_0) was obtained. The oxidation process causes a slight degradation of the micro- and mesopore structure and of the surface area. However, the number of adsorption centres, which are responsible for the adsorption of polar compounds, was increased by more than three times (Table 1.)

Purification of the used frying oil

The OPRARP oil sample was obtained by the treatment of the used oil OPR with a modified active carbon ARP. The purification process was carried out in the weight ratio 15:1. The oil sample and the adsorbent were mixed and next heated for 30 minutes at the temperature of 70 – 80°C. After this process, active carbon was separated from the oil through the filtration of hot suspension (about 60°C), with the use of the strainer working under 2 atm. pressure.

Analysis methods

The oil purification process was aimed to remove the lipids degradation products, which were formed during the frying of French chips: mainly polar compounds, and to evaluate the efficiency of the applied adsorbent. The following features were adopted to estimate the changes of oil properties under the frying and purifying conditions:

– colour, ±0.001[12],
– density ρ20, (pycnometer method, ± 0,0004 g/cm^3),
– viscosity η40, (Rheotest 3 apparatus, 60 s, 100 r.p.m, ± 0,01 Pa·s),
– iodine value IV, ±2.0 for IV ∈ <50; 100> and ±3.5 for IV∈ <100; 135>[13],
– acid value AV, ±3 %[14],
– peroxide value PV, ± 0.2 meq O_2/kg[15],
– anisidine value AnV, ±0.2[16],
– total oxidation index Totox[17],
– main fatty acids profiles determined by gas chromatography ±3% for compounds above 5% and ±0.2% for the compounds below 5%[18, 19],
– total polar compounds TPC, Oil Quality Tester – OIL METER FOM 200, ±2%.

The results of the measurements and calculations are shown in Table 2 and 3.

RESULTS AND DISCUSSION

During frying French chips in palm oil some unfavorable changes of the quality parameters occurred (Table 2.). The density, viscosity and the colour of the oil increased. The amount of the products of fatty acids hydrolysis – the free fatty acids' content (AV) was increased by almost 9 times. The

Table 2. The quality and the physicochemical properties of the oils under investigations

| Parameter	OP	OPR	OPRARP
Colour	50.7	88.7	39.0
$ρ^{20}$, g/cm^3	0.911	0.915	0.917
$η^{40}$, Pa·s	0.037	0.047	0.046
IV, $gI_2/100g$	60.98	56.45	57.10
AV, mgKOH/g	0.089	0.880	0.772
PV, milieq.O_2/kg	0.32	4.58	3.54
AnV	1.10	70.20	59.80
Totox	1.74	79.36	66.88
TPC, %	12.6	29.2	23.0

Table 3. The composition of fatty acid in the oil at various stages of purification and frying determined by gas chromatography [% wt.]

Fatty acids	OP	OPR	PRARP2
$C_{12:0}$	0.32	0.28	0.27
$C_{14:0}$	1.00	1.06	1.11
$C_{16:0}$	37.74	40.90	40.76
$C_{16:1 \ (cis-9)}$	trace	0.18	0.19
$C_{18:0}$	4.01	4.22	4.27
$C_{18:1 \ (cis-9)}$	44.50	42.64	42.63
$C_{18:1 \ (trans-9)}$	–	0.26	0.25
$C_{18:2 \ (cis-9, \ 12)}$	12.05	9.32	9.32
$C_{18:3 \ (cis-6, \ 9, \ 12)}$	0.45	0.41	0.38
$C_{18:3 \ (cis-9, \ 12, \ 15)}$	trace	0.23	0.24
$C_{20:1 \ (cis-11)}$	trace	0.24	0.25
$C_{20:2 \ (cis-11, \ 14)}$	–	0.25	0.32
$C_{20:3 \ (cis-8, \ 11, \ 14)}$	–	trace	trace
$C_{24:0}$	–	trace	trace
$C_{24:1 \ (cis-15)}$	–	–	–

„trace" – fatty acid's content: under the sensitivity threshold of the integrator (< 0,1%)

amounts of the oil oxidation products (PV) and the secondary oxidation products (AnV) increased by more than 13 and more than 62 times, respectively. In a similar way the frying process affects the total polar compounds content in oil (TPC) by about 130%. The content of unsaturated substances (IV) was reduced by about 7.5% (Fig. 1.)

The purification process using oxidised active carbon leads to an improvement of most of the quality parameters. Acid, peroxide and anisidine values, as well as the total polar compounds content, were reduced by about 12, nearly 23, almost 15 and more than 21%, respectively. The content of the unsaturated substances (IV) was increased by above 1%. The total oxidation index, after the adsorption process, was reduced, by almost about 16%. The biggest change occurred for the colour of the oil; purification by the oxidised active carbon treatment resulted in the parameter's improvement by more than 56% (Fig. 1.).
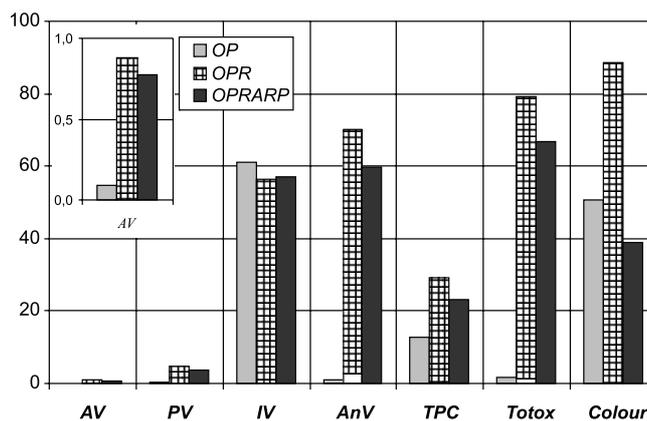
Figure 1. The quality parameters of the oil after each processing stage

During thermal processing in oil, changes occur in fatty acids profiles (Table 3 and 4.). The content of the saturated fatty acids (SFA) grew by about 8%. In that group, the amounts of palmitic ($C_{16:0}$) and stearic acids ($C_{18:0}$) increased by about 8 and 6.5%, in relation to fresh oil, respectively.

The amounts of unsaturated fatty acids: mono – (MUFA) and polyunsaturated fatty acids (PUFA) decreased by almost 3 and almost 18%, with reference to fresh medium (OP). The biggest changes in that group of fatty acids occurred in the contents of oleic ($C_{18:1 \, (cis-9)}$) and linoleic ($C_{18:2 \, (cis-9, 12)}$) acids. The contents of these unsaturated fatty acids were decreased from 44.5 to 42.6% and from 12.1 to 9.3%, respectively.

The adsorption process caused slight changes in the total content of saturated fatty acids (SFA) and polyunsaturated fatty acids (PUFA), whereas the content of monounsaturated fatty acids (MUFA) did not change. In fact, the purification process practically did not cause any improvement in the fatty acids content (Fig. 2, 3).
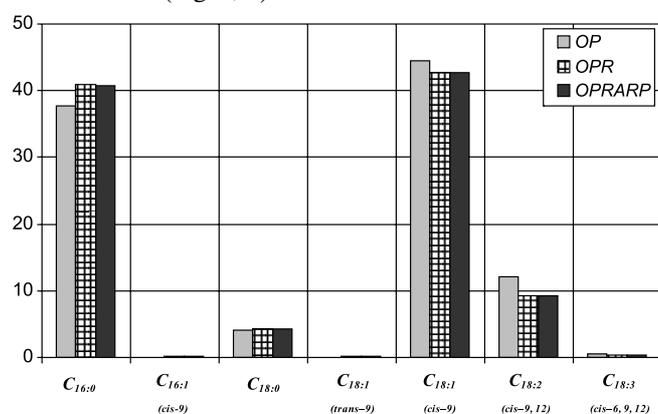

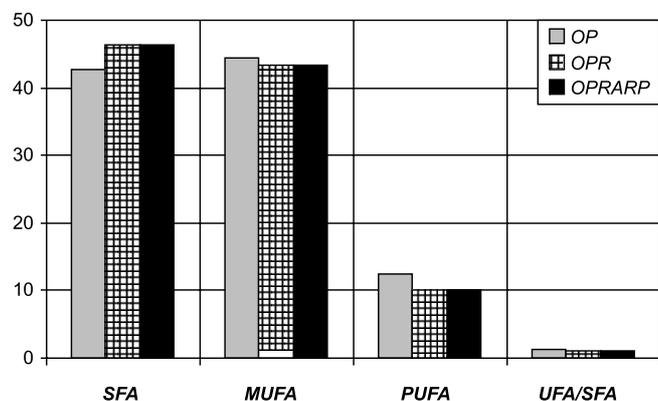**Figure 2.** The main fatty acid contents in the oil

Figure 3. A group of fatty acids and the ratio of the amount of unsaturated fatty acids to the saturated fatty acids in the oil, (SFA – saturated fatty acids, MUFA – monounsaturated fatty acids, PUFA – polyunsaturated fatty acids, UFA – unsaturated fatty acids)

SUMMARY

The investigation indicates that active carbon, modified by perhydrol treatment, influenced the quality and the physico-chemical properties of the used frying oil:

– active carbon with an oxidised surface character improves the properties of palm oil used for frying food – using relevant characteristic values,

– the ARP adsorbent purified the used frying oil from colour substances, lipid hydrolysis products, free fatty acids (AV), primary and secondary oxidation products (PV, AnV) and total polar compounds (TPC),

– the obtained adsorbent did not reduce the fatty acids content effectively,

– to improve the quality of the purification of palm frying oil, a more efficient adsorbent, which stops unfavorable fatty acids, needs to be applied.

SYMBOLS

SFA   – saturated fatty acids,
MUFA   – monounsaturated fatty acids,
PUFA   – polyunsaturated fatty acids,
UFA   – unsaturated fatty acids

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