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ATTEMPTS OF THE ELABORATION OF OPTIMAL CONDITIONS FOR FRYING OIL POLLUTANTS' ADSORPTION

INTRODUCTION

One of the most popular method of preparation food is deep frying in vegetable oils. Unfortunately a lot of them have a very poor thermostability caused by their chemical composition and they detoriate very fast. Nowadays, in Poland, fats used for frying have poor quality. That of course, causes shortage of time of their suitability to 40 - 60 hours (in our model frying of chickens and potato chips) [1, 2], whereas in other reports one can read about 100 or even 300 hours [3]. Disqualification moment of soya or rape oil in continuous chicken and chips frying appeared very quickly though the temperature was much lower (135 - 145°C) than mostly applied (180 - 185°C).

During deep frying a lot of degradation products are formed because of thermal oxidation, hydrolysis and polimerization, which results in off-flavors, darkening and foaming. Most of those compounds may be consumed with the fried food and therefore become dangerous components of consumers' diet [3, 4, 5, 6]. An increasing level of alkalic substances during frying causes the decrease of the interfacial tension around the food and thus allows the unpurified oil to get into the meal [7].

Because of the fact that a request for frying oils increases every year, there exists a problem of prolonging the period of their use through purification. For that purpose several experiments have been done. One of the method for keeping the oils' quality is a periodical addition of fresh oil. Another procedure of lower degradation of oil is filtration once a day. During last years several investigations have been done in which chemical adsorbents were applied [8, 9]. Addition of selective adsorbents or their mixtures improve the quality of oil by the reduction of the level of free fatty acids and colour compounds. Of course, one has to remember that the use of some selective adsorbents can cause decrease of oil stability.

Changes of physicochemical values of purified rape oil after chicken model frying (I oil)

Table 1

Kind of adsorbent (procedure)	Amount of adsorbent for 100 g of oil	Colour (orga-noleptic test)	% FFA	Decrease of FFA %	Iodine value (IV)	Decrease of IV %	Content of soap mg/kg of oil	Decrease of soap %	Colour test* with bromo-thymol indicator
Unpurified oil		yellow	1.60	–	97.85	–	17.25	–	violet
1. Active charcoal A silicagel	9 g 2 g	yellow	0.90	43.75	97.71	+0.14	1.88	89.10	green
2. Active charcoal B silicagel	3 g 6 g	dull yellow	1.05	34.38	95.17	+2.82	2.27	86.84	dark green
3. Active charcoal C	9 g	dull yellow	0.90	43.75	98.98	−1.14	9.08	47.37	yellow-green
4. Silicagel	2 g	orange	0.96	40.00	98.98	−1.14	12.49	27.59	dark green with violet glimmer
5. Diatemaceous earth	5 g	brown	1.10	31.25	92.63	+5.64	10.88	36.93	dark green with violet glimmer
6. Cellite	–	brown	1.05	34.38	92.63	+5.64	9.06	47.48	dark green
7. Bleaching clay Active charcoal Silicagel	2 g 9 g 2 g	brown	1.1	31.25	100.00	−3.11	0.00	100.00	–
8. No chemical adsorbent – degumming 75% H_3PO_4 – deacidification 4% NaOH with heating – rinsing with 1% NaCl – rinsing with H_2O – miscella phase 60% w/v in hexane – active charcoal	2 g	brown	0.85	46.88	100.25	−2.09	0.00	100.00	

* yellow colour – rape oil
violet colour – oil not for frying application

EXPERIMENTAL

Materials

Subjects of investigation were:

"I" — Universal rape oil, distributed by Kalisz Koncentrated Food Processing Plant „WINIARY" (PN.86/17-86908) applied to chicken model deep frying.

"II" — Universal rape oil (as above), taken from a restaurant after frying about 80 batches of chips in Predom-Zelmer frying pan equiped with thermostat, and then applied for deep frying of sausages.

Analytical methods for monitoring the quality of oils

— determination of free fatty acids (% FFA) according to AOAC (10); acidic value (AV) = % FFA × 1.99,
— determination of iodine value using Hanus method (PN-60/A-89914),
— determination of soap content (PN-70/A-86925),
— spectrophotometric determination of general colour of oil samples (BN-86/8050-30),
— measurement of viscosity at 40°C with Hoppler viscosimeter,
— determination of fatty acids composition using gas-chromatography AOAC (10),
— bromothymol blue colour test [1].

The efficiency of used adsorbents was expressed in percentage as the decrease of those values after whole purification procedure.

Kinds of adsorbents

a) powdered charcoal,
b) silicagel (from Schuchardt Munchen, 50 - 100 mesh),
c) diatomaceous earth,
d) bleaching clay Miltar-Standard,
e) cellite as the filtration aid material.

Purification procedures

100 g samples of oil I after model frying were weighed in 250 cm^3 beakers and stirred at the temperature 70 - 80°C for about 30 min. with different adsorbents or their mixtures according to following options:

1) Oil with the addition of active charcoal and silicagel — 9% and 2% w/w, respectively.
2) Oil with the addition of active charcoal and silicagel — 3% and 6% w/w, respectively.
3) Oil with the addition of active charcoal in amount of 9% w/w.
4) Oil with the addition of silicagel in amount of 2% w/w.

5) Oil with the addition of diatomaceous earth in amount 5% w/w. Another procedures are shown in table 1 at No 8.

Sampe oil II, taken from restaurant had a very high content of free fatty acids (% FFA=3,35, AV=6,67) several times more than accepted by norms (AV=1 - 2). The oil was burnt and therefore purified by degumming, dewaxing deacidification and miscella refining in hexane phase. In that results of work of Bhattacharyya and coworkers have been applied [11]. The specified stages of clearing procedures of restaurant oil and the appriopriate values of basic figures are presented in table 2.

Table 2

Stages of purification of II oil

Purification stages	% FFA	decrease of FFA%	peroxide value (PV)	iodine value (IV)	decrease of IV %
1. Directly after frying	3,35	–	3,2	78,7	–
2. Degumming with concentrated H_2SO_4 (0,5% v/v) with heating – desaponification with concentrated NaOH in miscella phase with hexane at 70°C – hot rinsing with 1% NaCl – hot rinsing with H_2O – removing of hexane	3,13	6,6	1,9	88,8	−12,8
3. – boiling with blenching clay – filtration through Cellite under vaccum	2,70	18,2	1,6	83,75	−6,4

RESULTS AND DISCUSSION

Complete process of clearing of the oil II, consisted of absolute precipitation of all soap, deviding the layers after rinsing, heating with adsorbent under the condenser, spinning and dribbling, almost in every case lasted very long (about 10 days). Of course it was also very hard to avoid degradation and desorption processes which may take place.

Efficiency of the method, expressed by decrease of % FFA, is also unsatisfied. Peroxide value (PV), applied in fat industry as the deodoration efficiency indicator [13] did not reach the value PV=0 (table 2).

Recovery of oil after all stages and expelling of hexane under vacuum reaches only about 50%.

Deacidification in miscella stage did not give the expected results — similar to those obtained by Bhattacharyya and coworkers [11], who converted the 30% FFA rise oil into a low amount of unsaponificable matter edible oil.

As far as oil I after the model frying is concerned, application of different adsorbents caused reduction of FFA, soaps and colour. Improvement of each value after the process was calculated for each parameters in percentage of decrease after purification procedure. It can be pointed out, that the best results were obtained for first three adsorption mixtures — procedure A, B, C (table 1), in which the addition of active charcoal and silicagel was applied. Decrease of FFA by 40% and soaps by 89% was obtained for 9g charcoal and 2g silicagel mixture per 100g of oil (table 1). Decrease of oil basicity was supported by colour test, in which an evident colour change of bromothymol blue indicator was reported (from yellow to green).

Spectrophotometric test of general colour also showed a significant improvement of this feature after purification (table 3).

Table 3

Spectrophotometric measurement of general colour of purified I oil (UV - VIS)

Kind of purified oil	Absorbance = = 460 nm ($21{,}8\ cm^{-1} \times 10^3$)	Absorbance = = 668 nm ($15\ cm^{-1} \times 10^3$)	General colour „C"	Iodine scale
1. Coarse oil ready for purification (46 h)	0.24	0.02	260	51
2. Oil + 9 g of active charcoal + 2 g of silicagel	0.055	0.02	75	28
3. Oil + 3 g of active charcoal + 6 g of silicagel	0.05	0.04	90	33
4. Oil + 9 g of active charcoal	0.065	0.04	105	35
5. Oil + 5 g of diatemaceous earth	0.13	0.26	390	61
6. Oil + 2 g of silicagel	0.24	0.035	275	54
7. Oil + Cellite (2×)	0.135	0.1221	257.1	50

Colour of oil was measured according to the formula:

$$C = 1000\ (A_{460} + A_{668})$$

where

A_{460} = value of absorbance of oil sample after diluting in CCl_4 (1/10 v/v) at $\lambda = 460$ nm

A_{668} = value of absorbance of oil sample after diluting in CCl_4 (1/10 v/v) at $\lambda = 668$ nm

Improvement of colour reached about 71% comparing it to the colour of oil after 46 hours — model frying. Similar results were achieved when active charcoal was applied (9g per 100g of oil - C). In this case the same reduction of FFA, smaller decrease of soap content (47%) and general colour (59,6%) was obtained. However poorer effect for diatomaceous earth was obtained. It was also found out that cellite — mainly used as a filtration aid, significantly improves quality of oil.

Addition of silicagel (2g per 100g of oil) causes rather considerable reduction of oil acidity (40%), what also confirms earlier investigations [8]. Also literature data concerning the increase of unsaturated fatty acids recorded as the decrease of iodine value, were corraborated. In our work in some cases that value was lower (table 1), probably because of adsorption of many polimerized or oxydized compounds. During purification one could observe the decrease of main three fatty acids in oil I (table 4). In the same time the improvement of the ratio

Table 4

Content of the fatty acids fraction of purified I oil

Kind of sample	Fatty acids						$\frac{\sum \text{unssaturated fatty acids}}{\sum \text{saturated fatty acids}}$
	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:0}$	
	1	2	3	4	5	6	
0	6.64	1.78	56.77	16.03	6.72	3.12	6.9
46 h	8.34	2.29	48.40	12.60	3.31	2.41	4.9
A	7.55	1.62	40.16	10.91	–	–	5.5
B	8.46	2.53	48.39	13.58	–	2.76	4.5
C	8.46	2.18	46.25	12.57	–	2.59	4.4

0 – fresh
46 h – unpurified oil after 46 hours chicken frying
A – oil purified by the mixture of active charcoal and silicagel (9 g and 2 g/100 g of oil accordingly)
B – oil purified by the mixture of active charcol and silicagel (3 g and 6 g/100 g of oil accordingly)
C – oil purified by active charcoal (9 g/100 g of oil)

of the sum of unsaturated acids to the sum of saturated ones for the best mixture of adsorbents (active charcoal and silicagel) was observed. With other adsorbents this value was similar to the one for fried oil.

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Even for model fried oil I purification in miscella stage (in hexane) did not give good results.

Miltar-Standard bleaching clay, normaly used in fat industry to obtain effect of oil decolourization, adsorption of soaps and phospholipides, was also applied for improving the quality of used frying oils. With this addition no trace quantity of soaps was reported, however the decrease of FFA, even with silicagel and active charcoal — table 1, was not satisfying (procedure 7). It was found that decrease of FFA reached only 31% while with silicagel and charcoal mixture it reached 44%. This can be explained probably by acidification caused by that adsorbent and therefore it can not support the conclusions of Platek and Wegrowski [12].

CONCLUSIONS

Of all tested adsorptive systems the best results were obtained when oil was treated by a mixture of active charcoal and silicagel — 3% and 2% (w/w), respectively. Degumming and desaponification in frying oil having about 1,5% FFA at the stage in hexane did not bring expected effects after chips and sausage deep frying when oil had more than 3% of FFA. Quite sufficient reduction of soap content, acidity and colour gave simple adsorptive systems (active charcoal and active charcoal with silicagel). Application of proposed simple procedures of oil purification gave expected results, however there still exists a problem of recuperation of purified oil. Even though this method was simplified, the efficiency reached only about 50% and thus it can be uneconomic in a practical use.

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PRÓBA OPRACOWANIA OPTYMALNYCH WARUNKÓW ADSORPCJI ZANIECZYSZCZEŃ Z OLEJÓW SMAŻALNICZYCH

Streszczenie

W pracy podjęto próbę wykorzystania olejów po smażeniu żywności poprzez adsorpcję produktów utleniania i polimeryzacji z wykorzystaniem chemicznych adsorbentów a także przez roztwarzanie olejów w rozpuszczalnikach organicznych. Oczyszczano olej pobrany z punktu gastronomicznego jak również inny, pochodzący z własnego wielogodzinnego modelowego smażenia kurczaków.

Oczyszczanie oleju w formie misceli w heksanie nie przyniosło spodziewanego efektu w przypadku oleju o zawartości wolnych kwasów tłuszczowych (FFA) powyżej 3%. Odśluzowywanie i wytrącanie mydeł w olejach smażalniczych o zawartości wolnych kwasów tłuszczowych około 1,5% jest niecelowe. Wystarczającą redukcję zawartości mydeł, kwasowości i barwy ogólnej dają zastosowane proste układy adsorpcyjne (węgiel aktywny i węgiel aktywny z żelem krzemionkowym). Najlepsze rezultaty uzyskano dla mieszaniny węgla aktywnego i żelu krzemionkowego dodanych do oleju w ilościach odpowiednio 9 i 12% w/w. W trakcie oczyszczania oleju zaobserwowano spadek zawartości trzech głównych

kwasów nienasyconych, ale jednocześnie nastąpiła poprawa stosunku sumy kwasów nienasyconych do sumy kwasów nasyconych dla najlepszego układu adsorpcyjnego. W pozostałych przypadkach wielkość tego stosunku była zbliżona do stosunku w oleju wyjściowym.

Zastosowanie ziemi bielącej Miltar-Standard najskuteczniej usuwa mydła, ale przyczynia się do zakwaszenia oleju.

Istnieje również problem z odzyskiwaniem oczyszczonego oleju. Nawet gdy procedura oczyszczania jest uproszczona wydajność kształtuje się tylko na poziomie 50%.

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ПОПЫТКА РАЗРАЪОТКИ ОПТИМАЛЬНЫХ УСЛОВИЙ АДСОРБЦИИ ЗАГРЯЗНЕНИЙ ИЗ МАСЕЛ ИСПОЛЬЗУЕМЫХ ДЛЯ ЖАРЕНЬЯ

Содержание

В работе предпринято попытку использования масел после жаренья пищи путём адсорбции продуктов окисления и полимеризации с использованием химических адсорбентов а также путём растворения масел в органических растворитегях. Очищалось масло взятое из пунктов общественного питания а также другое, взятое из собственного многочасового образцового жаренья цыплят.

Очистка масла в форме мисцеллы в гексане не дала ожидаемого эффекта в масле содержащем свыше 3% свободных жирных кислот (FFA). Очищение от слизи и оседание мыла в маслах используемых для жаренья, в которых содержится около 1,5% свободных жирных кислот, нецелесообразно. Достаточную редукцию содержимости мыл, кислотности и общей окраски приносят применённые простые адсорбционные системы (активированный уголь и активированный уголь с силикагелем). Наилучшие результаты были получены для смеси активированного угля и силикагеля добавленных в масло в соответственных количествах 9 и 2% в/н. Во время очистки масла замечено снижение содержания трёх главных жирных кислот, но одновременно произошло улучшение соотношения суммы ненасыщенных кислот к сумме насыщенных кислот дла наилучшей адсорбционной системы. В остальных случаях величина этого соотношения была приближена к соотношению к исходному маслу.

Применение выбеляющей земли Мильтар-Стандарт с наилучшим эффектом устраняет мыла, однако способствует закислению масла.

Выступает также проблема с получением обратно очищенного масла. Даже тогда когда процедура очищена упрощена, производительность составляет толко 50%.