__Original Research Article__

Study on the purification and reusability of burnt cooking oil and assessment of its physicochemical and safety parameters

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ABSTRACT

Aims: The aim of the study was to investigate the reusability of edible oils and to find which temperature the refined oils could be used for cooking purposes.
Study design: The study followed a completely randomized design (CRD).
Place and duration of study: The study was conducted at the Department of Agro Product Processing Technology and its corresponding laboratory on Jashore University of Science and Technology, Jashore, Bangladesh. The study took three consecutive months to complete the study.
Methodology: The study adopted several methods to refine the burnt cooking oils and analyze their physicochemical as well as cooking qualities. At first, the heat was applied to commercially purchased palm, soybean, and rice bran oil. Produced burnt oil was refined using a base and hexane mixture. After that, these refined oils were repeatedly heated for 15, 30 and 60 minutes and physicochemical quality like peroxide value (PV), saponification number (SN), acid value (AV), etc were analyzed for each oil sample at each time interval. Furthermore, cooking quality of the refined oils was determined by frying sausages using each oil and the flavor, color, texture and overall acceptability were determined using hedonic scale.
Results: The study found that the refining rate of each oil was at the peak when the base -to-hexane ratio was 9:1. An increasing trend was observed in the case of the peroxide value of the refined oils during repeated heating. This trend was most predominant in case of palm oil. In palm oil sample, PV of palm oil increased from 4.950±0.6 to 14.432±0.86 meqo$_2$/kg oil at the third time of heating. The other two sample oils also crossed the standard PV of the respective oil at the third time of heating. It means all the refined oil can be used for a maximum of three times. Acid value of the oils also showed the same trend of increasing with an increase in temperature. In the case of SN, palm oil showed a higher degree of saturation with increased heating time among the refined oils. The flavor, color, texture, and overall acceptability of the sausages fried in these three showed significant differences at $p<0.05$. This is an indicator that burnt cooking oil that was refined can be reused in cooking.
Conclusion: Due to the increasing price of edible oils and limited resources, they can be refined from their burnt stage and reused for cooking. Therefore, refining can be a good method to solving edible oil scarcity.

Keywords: Purification, reusability, burnt cooking oil, safety.

1. INTRODUCTION

Lipids are the most concentrated source of metabolic energy among carbohydrates, proteins, and lipids which are available through food to humans. Oils and fats contain more than twice the caloric value of equivalent carbohydrates or proteins. Their functional and textural characteristics contribute to the flavor and palatability of natural and prepared foods. They contain certain fatty acids which play an important role in nutrition and are also carriers of fat-soluble vitamins. The type of fat consumed plays a major role in the health of an individual as higher intakes of trans and saturated fats are known to have adverse effects such as promoting insulin resistance, inflammation, and increase in LDL (low-density lipoprotein) cholesterol, developing risk of diabetes and cardiac death [1] [2].

More than 90% of the world’s production of oil from vegetable, animal and marine sources is used as food or as an ingredient in food products. The beneficial applications of essential fatty acids like unsaturated fatty acids on human health have increased the market and market value of edible oils [3]. It has been proposed that an intake of 0.25 to 1.8 g of n-3 polyunsaturated fatty acids (PUFA), such as Eicosapentaenoic acid (EPA) and Docosahexaenoic acid (DHA) per day in the form of fatty fish or its supplements is adequate to elicit desirable benefits such as reducing platelet aggregation and lowering plasma triglycerides [4].

Vegetable oils and animal fats (meat, pork, etc.) are the major sources of dietary lipids. Palm, olive, soybean, sunflower, coconut, corn, cottonseed, and peanut are some of the oils of vegetable origin that are most widely used. According to the United States Department of Agricultural, the total oil production has increased from 140 million metric tons in 2010 to 161 million metric tons in 2013 to meet the demand. This imposes immense pressure on these oilseeds for the production of oils rather than any other uses.

Reusing edible oil for preparing food, particularly in deep-frying, is a common practice of food vendors to enhance profit. The oxidative degradation of oil accelerates during repeated heating and forms hazardous reactive oxygen species and also diminishing the natural antioxidant contents of the edible oil. During the deep frying of food, cooking oil is exposed to a very high temperature with the presence of moisture and air. Under such conditions, a series of complex chemical reactions take place, followed by loss of both quality and nutritional values of the cooking oil. Reusing of cooking oils initiates a series of chemical reactions, altering the fat constituents of cooking oil through polymerization, oxidation, hydrolysis, and isomerization, finally resulting in lipid peroxidation. Lipid peroxidation generates an extensive volatile or non-volatile component, including free fatty acids, trans isomers, ketones, aldehydes, alcohols, hydrocarbons, cyclic and epoxy compounds. As a consequence, when the same cooking oil is reused excessively, the chemical reactions increase to form dark color, off-flavor and increased viscosity. Hence, repeated use of the oil leads to the degradation of the cooking oil, both chemically and physically. The reused oil is called waste or burnt cooking oil.

Recycling burnt cooking oil can be a great alternative to reduce the production of oilseeds for oil manufacturing. And this can be applied for cooking purposes just like vegetable oil does. This is why our study aimed at the purification of some of the popular edible oils (Palm oil, Soybean oil, and rice bran oil) and the characterization of the oils after a successive degree of frying.

2. METHODOLOGY

2.1 Sample Collection and heating of oils

The experiment was performed using a Completely Randomized Design (CRD). Soybean, and Rice bran oil) were purchased from the super-shops of the locality of Jashore. The samples were heated until bluish smoke came out of the samples. All the heated oils then proceeded to the purification process.

2.2 Purification of the used oil

2.2.1 Preparation of 2N sodium hydroxide solution

80 gm Sodium hydroxide pellets were taken in a 1 Litre beaker and 1 Litre distilled water was added to prepare a 2N Sodium hydroxide solution. The mixture was agitated to mix the pellets thoroughly. Then the solution was transferred into a volumetric flask and covered with a lid. All the chemicals used were of AR Grade.

2.2.2 Refining of the burnt cooking oils

Five milliliters of hexane was added with 15 ml of burnt cooking oil (sample) in a closed-lid vessel using the pipette. Then the mixture was taken in the vortex machine to agitate for 1 minute to mix properly. After removing the mixture from the vortex, 9 ml 2N Sodium hydroxide and 1-2 drops of phenolphthalein indicator were added to the mixture. Soap-like precipitation was observed at the top of the vessel. After that, water was taken into a beaker and heated on the burner. The vessel was dipped into the water for uniform heating. After heating, two layers were observed. The upper layer consisted of oil and hexane was separated by a dropper, and the bottom layer which consisted of water and other foreign matters was discarded. The separated oil and hexane mixture were poured into a beaker and heated in a burner to remove the hexane from the mixture. Air was supplied to the beaker by electric means to flow off the hexane gathered at the upper portion of the beaker after heating. When all the hexane was blown away, the oil was fully refined. This procedure was followed for oil samples.

2.2.3 Decolorization of refined cooking oil

A filter paper was placed in the filter funnel. About 5 gm of activated charcoal was weighed and poured on the filter paper. Untreated refined oil was passed through the activated charcoal filter to decolorize the produced refined oil.

2.3 Heating of the refined oils

An aliquot of refined oil (1L) was separated and labeled as unheated cooking oil (UHCO). Another aliquot of each oil (1L) was heated (above 300°C) above its smoke point for 30 min and then was cooled to room temperature. From this, a sample of 1L was separated and labeled as singly heated cooking oil (SHCO). The same process was repeated to obtain oil heated 3 times (3RHCO). This process of heating and cooling the oil was performed without the addition of fresh oil. The viscous dark brown oil sample thus obtained was then stored in amber color bottles to prevent the photodegradation of PAHs [5].

2.4 Characterization of the refined oils burnt in different degrees

The three oil samples were analyzed according to official methods described by [6] including peroxide value, saponification number, iodine value, acid value, etc. to evaluate their degree of deterioration.

2.4.1 Peroxide Value

5g refined oil was weighed and taken into a conical flask. 25 ml of ethyl acetate solvent was added and the air above the liquid was displaced with CO_2. 1 ml of the potassium iodide solution was added in the flask with a stopper and it was allowed to stand for 1 minute (with shaking). Then 35 ml of water was added and the liberated iodine was titrated with 0.1 N sodium thiosulphate solution using starch as an indicator. The conical flask was vigorously shaken at the end to remove the last traces of iodine from the chloroform layer. A blank titration was carried out simultaneously. (The thiosulphate consumption should be negligible) The peroxide value was determined using the following formula:

$$\text{Peroxide value} = \frac{(\text{Sample titer} - \text{Blank titer}) \times \text{Normality of sodium thiosulphate solution} \times 1000)}{\text{weight of the fat taken}}$$

2.4.2 Saponification number

The sample was filtered. It ensured that the sample was free of impurities and moisture. 1 gm of the sample was weighed in a 250 ml conical flask. 25 ml of alcoholic KOH solution was pipetted and a few glass beads or pieces of pumice were added. The flask was connected to an air condenser of at least 65 cm (or preferably 202 cm) long. The sample was reflasked on a water bath or a hot plate for not more than 1 hour. Gently but steadily the sample was boiled until it was saponified as indicated by the absence of oily matter and the presence of a clear solution appeared. The flask and the condenser were allowed to cool. The inside of the condenser was washed with about 10 ml of hot ethyl alcohol neutral to phenolphthalein. 1 ml of phenolphthalein indicator was added and titrated with standard HCl. A blank determination was conducted alongside.The saponification number were determined using the following formula:

$$Saponification\ number = \frac{(\text{Blank titer} - \text{Sample titer}) \times \text{Normality of KOH solution} \times 56.01}{\text{Weight of sample (gm)}}$$

2.4.3 Iodine Value

0.6 gm of refined oil was weighed accurately into a clean dry 250 ml glass stoppered conical flask, and 10 ml of carbon tetrachloride was added. 25 ml of Wij's solution was added, mixed and stored in a dark cupboard for 30 min. 15 ml of 10% potassium iodide solution and 100 ml of distilled water were added. The solution was titrated with 0.1 N $Na_2S_2O_3$ solution using starch as an indicator near the endpoint. A blank determination was carried out without the sample. The iodine value of the oil samples was measured using the following formula:

$$\text{Iodine value} = \frac{\text{Blank determination} - \text{Sample determination}) \times \text{Normality of Sodium thiosulphate} \times 12.69}{\text{Weight of sample (gm)}}$$

2.4.5 Acid Value

10 gm of sample was weighed. The sample was dissolved in hot 100 ml of neutralized ethanol and was titrated using 0.1 N alkali using phenolphthalein as an indicator. The conical flask was shaken vigorously during titration and the solution was kept warm. The acid value of the oils was calculated using the below-mentioned formula:

$$\text{Acid value} = \frac{\text{ml of alkali} \times \text{Normality of alkali} \times 56.01}{\text{Weight of sample (gm)}}$$

2.5 Analysis of cooking quality of refined oil

Refined oils are used in the preparation of fried sausage to analyze their cooking quality. The three types of oil that were refined were used separately for the preparation of fried sausage. Sensory evaluation of sausage fried using three different oil were done by taste testing panel. The taste testing panel was made up of 10 test panelists. They were asked to evaluate flavor, color, texture, and overall acceptability by a scoring rate on a 9-point hedonic scale where the scores represented the followings: 9= Like extremely, 8=Like very much, 7= Like Moderately, 6= Like slightly, 5= Neither like nor dislike, 4= Dislike slightly, 3= Dislike Moderately, 2= Dislike very much and 1= Dislike extremely.

2.6 Statistical Analysis

All the data found in the study were statistically analyzed using SPSS software version 25 to determine the level of its significance at $P<0.05$.

3. RESULTS AND DISCUSSION

3.1 Refining rate of the burnt cooking oils

Total of 2000 ml of waste cooking oil was refined taking 15 ml each time. Among the oil samples, it was observed that the refining rate was highest for the base-to-hexane ratio of 9:1. The refining rate reduced gradually after the peak. It happened due to the gradual increase of the base, although the amount of hexane remained constant. And as hexane binds with the oil here, using an increased amount of base can't refine an increased amount of oil. Figure 1 depicts the refining rate of soybean oil with respect to the base-to-hexane ratio. The other two oils also show the same results which are presented in Table 1.

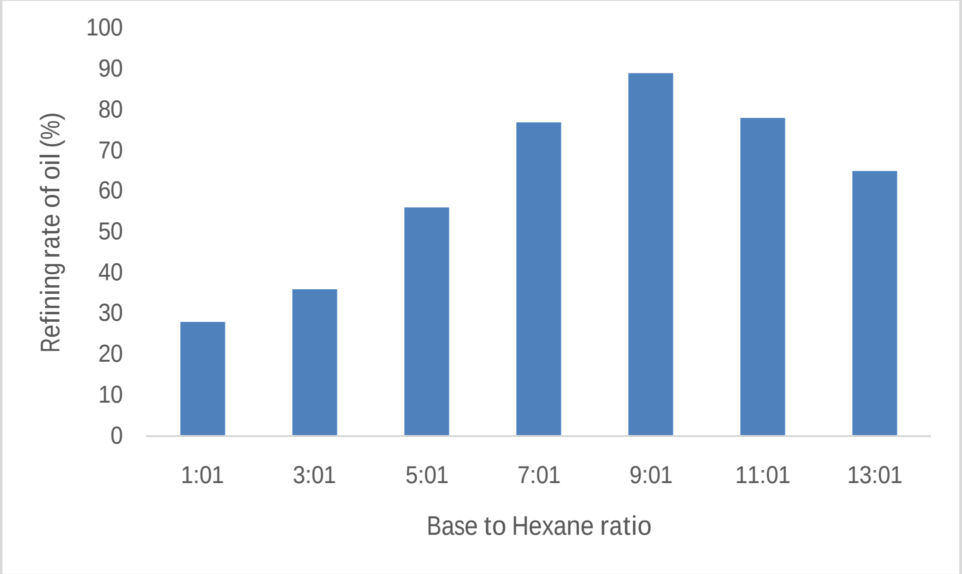

Figure 1: Refining rate of soybean oil with respect to base-to-hexane ratio

Table 1. Refining rate of oils with respect to base to hexane ratio

Base to hexane ratio	**Refining rate of oils (%)**		
	Palm oil	Soybean oil	Rice Bran oil
1:1	22	28	29
3:1	29	36	32
5:1	47	56	49
7:1	61	77	62
9:1	85	89	81
11:1	80	78	78
13:1	69	77	72

3.2 Chemical analysis of refined cooking oil

3.2.1 Peroxide Value

The peroxide value of oil is used to determine the autoxidation of oil due to external or internal changes in the chemistry of the oil, generally by heating. According to [2], [7] and [8] standard peroxide value for palm oil, soybean oil and Rice bran oil is 1.03, 1.79, and 0.56 meqO_2/kg respectively.

The maximum peroxide value level of refined oil suggested by [9] is up to 10 meqO_2/kg. Beyond this oxidation starts in the oil and forms free radicals. From Table 2 it is seen that for each oil, after 3rd time of heating the value exceeds the standard value. So, it can be said that the oil that was refined in this experiment could be used for a maximum of three times for cooking.

Table 2. Peroxide value of the refined oils heated at different degrees of time

Time of heating (minutes)	Peroxide Value (mEqO$_2$/kg) (mean±SD)		
	Palm oil	Soybean oil	Rice Bran oil
0	4.950±0.6	4.501±0.23	2.185±0.45
15	7.975±0.42	6.391±0.54	5.917±0.33
30	10.924±0.98	9.765±0.32	6.703±0.67
60	14.432±0.86	12.974±0.56	9.630±0.87

3.2.2 Saponification number

A study performed by [10] revealed the heating effect on the saponification number of palm, coconut and groundnut oil. In all the cases, at the first degree of heating, the saponification number increased significantly. In our study, the saponification numbers also followed the same trend and increased significantly ($p<0.05$). High saponification number is an indication of higher degree of unsaturation. Followed by the second- and third-time heating, the saponification number started to fall down and this decrease in saponification number was predominant in palm and soybean oil. A similar study by [11] reported the continuous decrease in saponification number. In Table 3, it could be observed that both soybean and rice bran oil maintained the standard declared by [12] which was 181 ± 2.60 mEqO$_2$/kg. But in case of palm oil, it exceeded the standard value which also means that it followed a high degree of saturation with increase in heating time.

Table 3. Saponification number of the refined oils heated at different degrees of time

Time of heating (minutes)	Saponification number (mEqO$_2$/kg) (mean±SD)		
	Palm oil	Soybean oil	Rice Bran oil
0	192±0.89	187±0.23	184.87±0.56
15	194.76±0.31	189.62±0.54	187.98±0.87
30	184.24±0.44	185.76±0.32	185.87±0.56
60	180.35±0.60	181.56±0.45	182.34±0.77

3.2.3 Iodine Value

Results depicted on the Table 4 indicates that the iodine value of all three oils decreased with the increased heating time. But it is more significant in the case of rice bran oil. The IV of rice bran oil at the unheating stage was 100.125±0.45 mEqO2/kg. It started to decrease and the rate of decrease was higher (about 77%) than that of the other two oils. This may be due to the double bonds present in rice bran oil. Similar findings were reported by [13].

Table 4. Iodine value of the refined oils heated at different degrees of time

Time of heating (minutes)	Iodine value (mEqO$_2$/kg) (mean±SD)		
	Palm oil	Soybean oil	Rice Bran oil
0	49.54±0.6	189.551±0.65	100.125±0.45
15	47.975±0.43	187.198±0.99	98.097±0.76
30	47.912±0.98	186.675±0.65	96.873±0.56
60	45.321±0.78	185.974±0.56	92.340±0.87

3.2.4 Acid value

The acid value of all three oils presented on table 5 increased significantly ($p<0.05$) which indicates that the amount of free fatty acids increases with an increase in heating time. Similar findings were reported by [14].

Table 5. Acid value of the refined oils heated at different degrees of time

Time of heating (minutes)	Acid value (mEqO$_2$/kg) (mean±SD)		
	Palm oil	Soybean oil	Rice Bran oil
0	10.54±0.63	0.58±0.54	1.23±0.45
15	12.975±0.43	0.62±0.23	1.54±0.16
30	14.242±0.98	0.65±0.32	1.55±0.56
60	15.341±0.74	0.74±0.56	1.58±0.37

3.3 Analysis of cooking quality of refined oil

The cooking quality of refined oils was analyzed on the basis of flavor, color, texture and overall acceptability of the sausages fried using them. The results of analysis of variance (ANOVA) in table- 6, 7, 8, 9 showed that the sausage cooked using palm, soybean and rice bran oil were significantly different ($p<0.05$). These results depicted the suitability of the refined oil in daily household cooking.

Table 6: Analysis of variance (ANOVA) for the flavor of sausage fried from different oils

ANOVA Source of variation	SS	df	MS	F	P-value	F
Between Groups	10.06667	2	5.033333	8.882353	0.001086	5.488118
Within Groups	15.3	27	0.566667			
Total	25.36667	29				

Table 7. Analysis of variance (ANOVA) for color of sausage fried from different oils

ANOVA Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	38.9	3	12.96667	4.145648	0.012706	2.866266
Within Groups	112.6	36	3.127778			
Total	151.5	39				

Table 8. Analysis of variance (ANOVA) for the texture of sausage fried from different oils

ANOVA Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	38.9	3	12.96667	4.314233	0.010669	2.866266
Within Groups	108.2	36	3.005556			
Total	147.1	39				

Table 9. Analysis of variance (ANOVA) for the overall acceptability of sausage fried from different oils

ANOVA Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	45.675	3	15.225	5.117647	0.004729	2.866266
Within Groups	107.1	36	2.975			
Total	152.775	39				

4. CONCLUSION

The reusability of oil was the prime concern of the study. Oils burnt in different times of heating were refined and the best base-to-hexane ratio used were studied. The base-to-hexane ratio 9:1 refined the most amount of oil irrespective of the type. The chemical quality analysis revealed the effect of heating on the physicochemical quality of the refined oils. Peroxide value and acid value increased with increased time of heating. Peroxide value of oil samples were above [10] standard of 10 meqO_2/kg oil. The saponification number of all three oils increased at first degree of heating. After that, the saponification number started to decrease with continuous heating. In case of palm oil, the saponification number decreased significantly and crossed the permitted value stated in [13]. It revealed that with continuous heating palm oil is prone to high degree of saturation. All of the oils' iodine values demonstrated a tendency to decline during the course of continuous heating, although rice bran oil exhibits this trend the most. It could be as a result of the double bonds being more prevalent in rice bran oil than in palm or soybean oils. A hedonic scale of 0–9 points was used to evaluate the oils' suitability for cooking. Analysis of variance was used to compare the flavor, color, texture, and overall acceptability of sausage made with three different refined oils, and the findings revealed that each oil had a substantial impact on each of the criteria. By frying various food products in the oils and evaluating their physicochemical quality with each degree of heating that the oils get, further examination of the oils' cooking quality may be done.

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