Characterization of Palm Fatty Acid Distillate of Different Oil Processing Industries of Pakistan

Abdul Sattar Chang1,2, Syed Tufail Hussain Sherazi1, Aftab Ahmed Kandhro2, Sarfaraz Ahmed Mahesar1*, Fouzia Chang1, Syed Nasrullah Shah1, Zahid Hussain Laghari1 and Tarique Panhwar1

1 National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro -76080, PAKISTAN
2 Dr. M. A. Kazi Institute of Chemistry, University of Sindh, Jamshoro -76080, PAKISTAN

Abstract: Palm fatty acid distillate (PFAD) is cheap and valuable byproduct of edible oil processing industries. This study was designed to characterize PFAD collected from different local oil industries. AOCS methods were used for the determination of physicochemical parameters such as free fatty acid (FFA), saponification value (SV), iodine value (IV), peroxide value (PV) and moisture content. Fatty acid composition was analyzed using GC-MS. Moisture content of samples was found to be in the range between 0.06-7.50%, while FFA, SV, IV and PV were found to be 65.70-94.68%, 195.23-219.64 mg KOH/g, 38.49-63.10 g I2/100 g, 1.09-16.50 meq/kg, respectively. Mean value of fatty acids in PFAD was found as 0.04% lauric, 0.42% myristic, 41.25% palmitic, 7.29% stearic, 41.58% oleic, 8.95 % linoleic, 0.04% eicosenoic, 0.27% arachidic, 0.07% docosanoic, and 0.05% tetracosanoic acid, respectively. Palmitic acid was found as dominant saturated fatty acid 38.63-45.30%, whereas oleic acid C18:1 ω9 was major unsaturated fatty acid 33.54-44.05 % in PFAD.

Key words: palm oil, deodorizer distillate, chemical characterization, fatty acid composition

1 Introduction

Palm oil is obtained from fruits of oil palm tree (Elaeis guineensis). There are two different types of oils extracted from palm fruit. One type of oil is obtained from mesocarp part of palm fruit known as crude palm oil (CPO) and other obtained from the kernel of the fruit palm and known as palm kernel oil (PKO)1,2. Both CPO and PKO have their own importance, characteristics and commercial value3. Due to distinct fatty acid composition (FAC) and triacylglycerol (TAG) profile CPO has many food applications. Generally palm oil contains about 1% phytochemicals such as vitamin E (600-1000 ppm), carotenoid (500-700 ppm), phytosterols (300-620 ppm), squalene (250-540 ppm), phospholipids (20-100 ppm), co-enzyme Q10 (10-80 ppm) and polyphenolics (40-70 ppm)4.

Crude palm oil is not directly used for edible applications but it is refined in order to remove undesirable components such as free fatty acids (FFAs), partial acylglycerides, metals, colored compounds, odorous substances5. Refining of crude oil is carried out by either physical refining or chemical process. In physical refining FFAs are removed by distillation, while in chemical refining FFAs are removed by chemical neutralization (alkali neutralization). Refining process involves degumming, neutralization, bleaching and deodorization. Last step of refining is deodorization which is carried out through vacuum distillation. This is very important step in which odorous components and also FFAs are removed. As a result, deodorizer distillate (DD) is produced which contains FFAs and some minor components such as tocopherols, squalene, and phytosterols. DD is the most important byproduct obtained and considered as the cheap source of FFAs and other minor valuable components such as squalene, hydrocarbons, phytosterols tocopherols, tocotrienols, mono and di-glycerides6. Quantity of palm oil DD is usually about 4-5% depending on the level of FFAs in CPO7,8. In one reported study, PFAD was found to be 96.1% of FFAs and glycerides and other minor components squalene (0.76%), tocopherols and tocotrienols (0.48%), phytosterols (0.37%), and hydrocarbons (0.71%)9. PFAD and DD obtained from deodorization of other vegetable oils have been used for production of biodiesel due to presence of high concentration of FFAs10-12. Due to presence of tocopherols and phytosterols, PFAD has also many other applications in foods and cosmetics in-
PFAD has been widely used in non food industries such as oleochemical industries as well as in preparation of feed and soap. There is growing trend to utilize cheap byproducts of industries to prepare valuable products for commercial purpose and value addition. Focus of today’s scientists is on the natural materials in place of synthetic materials to fulfill the health and environmental obligations. DD is readily available source of bioactive components for the production of biodiesel, polyols and other valuable products of industry. To find proper use of PFAD, it is essential to characterize its composition. Therefore, aim of present study is to characterize PFAD obtained from different edible oil industries for their fatty acid composition and other physicochemical parameters.

2 Materials and methods

2.1 Reagents and sample collection

All chemicals, reagents and solvents used were from E. Merck (Darmstadt, Germany). Fatty acids methyl esters (FAME) standards (GLC 481-B) were purchased from Nu-Chemcheck Prep., Inc. (Elyrian, MN). Two PFAD samples were collected on different dates from batches of five different palm oil processing industries located at Hyderabad and Karachi, Pakistan. All the samples were stored in the refrigerator at 4°C till further analysis.

2.2 Physicochemical Parameters

All the physicochemical parameters such as moisture content, FFA, IV, PV and SV of the PFAD samples were determined by official AOCS methods.

2.3 Moisture content

The moisture content of PFAD was determined using AOCS official method Aa 3-38. Sample of PFAD (5 g) was heated in an oven (Memmert, Schwabach, Germany) at 105°C for 3 hours.

2.4 Free fatty acid value

Amount of FFA in PFAD was determined using AOCS official method Aa 6-38. Titration of sample was performed against the standardized aqueous solution of sodium hydroxide. About 1 g PFAD sample was placed in a 250 mL conical flask which contained 20 mL of neutral ethanol. The mixture was heated, shaken and titrated against 0.1 N sodium hydroxide in the presence of phenolphthalein indicator.

2.5 Iodine value

The IV of PFAD was determined using AOCS official method Cd 1-25. Iodine value indicates the presence of unsaturation in oil or fat. PFAD was put in conical flask containing carbon tetrachloride (15 mL), Wij’s reagent (25 mL) and solution of potassium iodide (5%). Solution was kept in dark for 30 min and liberated iodine was titrated against 0.1 N standard sodium thiosulphate solutions using starch as indicator.

2.6 Saponification value

AOCS official method Cd 3-25 was used for the determination of SV. About 2 g of PFAD was taken in round bottom flask and refluxed for 60 min in the presence of 25 mL of 95% ethanolic potassium hydroxide. In the end titration was carried out against standardized solution of 0.5 N hydrochloric acid using phenolphthalein as indicator.

2.7 Peroxide value

PV was determined using AOCS official method Cd 8-53. About 2 g of PFAD was dissolved in 15 mL mixture of glacial acetic acid and chloroform (3:2 v/v%). Resulting solution was titrated against standardized solution of sodium thiosulphate (0.1 N) using starch (1%) as indicator.

2.8 Determination of fatty acid composition

Before the determination of fatty acid composition, fatty acids methyl esters (FAMEs) were prepared using standard IUPAC method 2.301. Agilent 6890 N gas chromatograph instrument coupled with an Agilent MS-5975 inert XL mass selective detector and an Agilent auto sampler 7683-B injector (Agilent Technologies, Little Fall, NY, USA) was used in this study. The ChemStation 6890 Scale Mode software was used for peak analysis. A capillary column HP-5MS (5% phenyl methyl siloxane) with column length 30 m, i.d 250 μm, film thickness 0.25 mm was used for the analytical separation of fatty acids. Initial Oven temperature was 150°C maintained for 2 min then raised to 220°C at ramp rate of 4°C/min. Helium was used as carrier gas with flow rate of 0.8 mL/min. Injector and detector temperature was set at 240 and 270°C, respectively. 1 μL quantity of each sample was injected into the column in split mode. Mass detector was operated with an electron impact (EI) ion source mode at 70 eV with scan range of 50-550 m/z. Two libraries (NIST and Wily) were used for the identification of fatty acids in PFAD samples.

2.9 Statistical Analysis

Identification of fatty acids in PFAD samples were performed by retention time and comparison of mass spectra of known FAME standards (palmitic, oleic, stearic and linoleic acid) with GC-MS libraries. Two batches of each five PFAD samples at different processing dates were collected and analyzed three times and data was reported as mean with the standard deviation (SD) \(\bar{x} = 2 \times 5 \times 3\).
3 Results and discussion

3.1 Physicochemical parameters

Table 1 represents the physicochemical parameters of PFAD samples obtained from different edible oil industries such as moisture content, FFA, IV, PV and SV. All samples were reddish brown semisolid at room temperature. Moisture content of PFAD samples were found to be in the range between 0.06-7.50%. Maximum moisture found to be 7.5% which was higher than previous findings[17]. FFA content ranged between 65.70-94.68% with mean value of 80.19%, which was lower than reported FFA values[17, 18]. Higher mean FFA value (94.68%) was observed for PFAD-2 and lower for PFAD-1 (65.70%). FFA content of PFAD-1 in current study was found to be lowest from earlier reported values.

IV is another parameter which indicates the unsaturation in oil and fat[15]. In this study, IV was found in the range of 38.49-63.10 g I2/100 g with mean value of 51.24 g I2/100 g. IV found in this study was lower than reported studies[17, 20]. PV indicates about the oxidation level of oil and fat with the formation of peroxides and hydroperoxides. PV values for PFAD-1 (16.50 meq/kg) and PFAD-5 (10.16 meq/kg) were found to be higher than earlier study[21], while PV values for PFAD-2, PFAD-3, and PFAD-4 were found to be comparable to previous reported values. Range of SV in this study was found to be 195.23-219.64 mg KOH/g with mean value of 205.71 mg KOH/g which was slightly lower than one published data[27] and similar to other study reported by Moh et al.[18]. SV of PFAD samples is important parameter which is often applied in soap and cosmetic industries[23].

3.2 Fatty acid composition

Fatty acid composition of PFAD assesses its possible use in industrial sector such as energy, cosmetic and soap manufacturing industries[23]. Fatty acid composition of PFAD samples was determined using GC-MS after preparing methyl esters. Table 2 shows the fatty acids composition as a mean values with their standard deviations. Fatty acids profile of PFAD samples includes lauric acid (C12:0), myristic acid (C14:0), palmitic acid (C16:0), stearic acid (C18:0), two isomers of oleic acid (C18:1 n9 and C18:1 n11), linoleic acid (C18:2 n9,12), eicosanoic acid (C20:1 n11), eicosanoic acid (C20:0), docosanoic acid (C22:0) and tetracosanoic acid (C24:0). Palmitic acid (C16:0) was found to be dominant saturated fatty acid in all PFAD samples ranging from 38.63-45.30%. Among the unsaturated fatty acids oleic acid (C18:1 n9) was found to be main fatty acid ranged between 33.54-44.05%. Oleic acid (C18:1 n9) in present PFAD samples was found higher than earlier reports[7, 18].

Table 3 represents the important groups and ratios of fatty acids in PFAD. Saturated fatty acids (SFA) and unsaturated fatty acids (USFA) content of samples were found in the range of 46.28-55.82% and 44.12-53.57%, respectively. Among the USFA, monounsaturated fatty acids (MUFA) and poly unsaturated fatty acids (PUFA) were in the range between 33.94-44.35% and 7.57-10.18%, respectively. Linoleic acid (C18:2 n9,12) was the only PUFA found in

Table 1  Physicochemical characteristics of PFAD.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PFAD-1</th>
<th>PFAD-2</th>
<th>PFAD-3</th>
<th>PFAD-4</th>
<th>PFAD-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical Appearance</td>
<td>Reddish brown semisolid</td>
<td>Reddish brown semisolid</td>
<td>Reddish brown Semisolid</td>
<td>Reddish brown semisolid</td>
<td>Reddish brown semisolid</td>
</tr>
<tr>
<td>Moisture Content (%)</td>
<td>7.90-17.19</td>
<td>7.50-0.20</td>
<td>7.50-0.20</td>
<td>7.80-0.86</td>
<td>8.83-0.12</td>
</tr>
<tr>
<td>FFA (%)</td>
<td>65.50-60.90</td>
<td>65.70-1.10</td>
<td>93.22-95.55</td>
<td>94.68-2.50</td>
<td>84.35-86.50</td>
</tr>
<tr>
<td>IV (g/100 g)</td>
<td>62.42-64.12</td>
<td>63.10-1.40</td>
<td>37.79-39.28</td>
<td>38.49-1.30</td>
<td>49.29-51.24</td>
</tr>
<tr>
<td>PV (meq/kg)</td>
<td>15.89-17.19</td>
<td>16.50-0.20</td>
<td>1.02-1.16</td>
<td>1.09-0.02</td>
<td>3.05-3.51</td>
</tr>
<tr>
<td>SV (mgKOH/g)</td>
<td>207.80-212.10</td>
<td>209.70-2.50</td>
<td>205.10-206.30</td>
<td>206.30-8.68</td>
<td>198.26-202.56</td>
</tr>
</tbody>
</table>

Table 2  Fatty acid composition of PFAD.

<table>
<thead>
<tr>
<th>Fatty Acid (%)</th>
<th>PFAD-1</th>
<th>PFAD-2</th>
<th>PFAD-3</th>
<th>PFAD-4</th>
<th>PFAD-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric acid C12:0</td>
<td>0.001-0.03</td>
<td>0.01-0.00</td>
<td>0.002-0.09</td>
<td>0.04-0.00</td>
<td>0.001-0.08</td>
</tr>
<tr>
<td>myristic acid C14:0</td>
<td>0.02-0.05</td>
<td>0.26-0.00</td>
<td>0.01-0.95</td>
<td>0.28-0.00</td>
<td>0.15-1.50</td>
</tr>
<tr>
<td>Palmitic; C16:0</td>
<td>36.99-39.97</td>
<td>38.63-1.5</td>
<td>45.91-46.87</td>
<td>45.30-1.30</td>
<td>39.94-41.68</td>
</tr>
<tr>
<td>Stearic; C18:0</td>
<td>8.02-8.17</td>
<td>8.07-0.24</td>
<td>9.38-10.5</td>
<td>9.87-0.22</td>
<td>5.12-6.97</td>
</tr>
<tr>
<td>Oleic; C18:1 n9</td>
<td>4.32-45.65</td>
<td>44.05-1.20</td>
<td>33.12-34.82</td>
<td>33.54-1.30</td>
<td>41.21-42.46</td>
</tr>
<tr>
<td>Oleic; C18:1 n11</td>
<td>0.12-0.35</td>
<td>0.25-0.00</td>
<td>0.21-0.56</td>
<td>0.37-0.01</td>
<td>0.51-1.54</td>
</tr>
<tr>
<td>Linoleic; C18:2 n9,12</td>
<td>7.78-8.95</td>
<td>8.46-0.22</td>
<td>9.55-10.83</td>
<td>10.18-0.34</td>
<td>8.70-9.87</td>
</tr>
<tr>
<td>Eicosanoic; C20:1 n11</td>
<td>ND</td>
<td>ND</td>
<td>0.01-0.06</td>
<td>0.03-0.00</td>
<td>0.10-0.18</td>
</tr>
<tr>
<td>Arachidic acid C20:0</td>
<td>0.014-0.21</td>
<td>0.11-0.00</td>
<td>0.11-0.45</td>
<td>0.21-0.00</td>
<td>0.31-0.56</td>
</tr>
<tr>
<td>Docosanoic acid (C22:0)</td>
<td>0.07-0.10</td>
<td>0.09-0.00</td>
<td>0.047-0.16</td>
<td>0.12-0.00</td>
<td>0.04-0.09</td>
</tr>
<tr>
<td>Tetracosanoic acid (C24:0)</td>
<td>0.05-0.09</td>
<td>0.07-0.00</td>
<td>ND</td>
<td>0.05-0.08</td>
<td>0.07-0.00</td>
</tr>
</tbody>
</table>

ND, not detected
samples of PFAD. Ratio of saturated to unsaturated fatty acids (SFA/UFA) represents the relation between two major fatty acid groups and the value varies from 0.86 to 1.27. These values showed that there was high proportion of SFA, as all samples belong to PFAD.

4 Conclusion

Fatty acid composition and physicochemical parameters of PFAD from different Pakistani oil industries were checked and compared with reported studies. Composition of PFAD varies and depends upon quality of crude palm oil and on the processed conditions at which it was refined. Overall, PFAD samples showed mixed behaviors with already reported studies. Some parameters of PFAD samples were found to be different while some were comparable to other published data. Palmitic acid and oleic acid were the dominant fatty acids. Unsaturated fatty acids could be separated and utilized in production of many industrially important products.

References:


