Kinetics of the Change in the Acid Value of Palm Oil during Simulated Deep Frying

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The deterioration of palm oil during deep frying was mainly examined at 180°C by measuring the acid value (AV) of the oil to which water was continuously fed at a constant rate. The addition of water simulated importing water from the material being fried. In most cases, the AV rapidly increased after an induction period, reached a plateau, and then gradually decreased in most cases. The addition rate of water significantly affected the change in the AV. The changes in the AV were also examined for the mixtures of the constituent fatty acids of palm oil with or without glycerol. Based on these experimental results, a kinetic model was proposed for describing the change in the AV during deep frying. The rate constants of the model were evaluated at various feed rates of water. The rate constant for the degradation of the AV-positive compound scarcely depended on the feed rate of water, but the rate constants for the hydrolysis and reverse-hydrolysis of the ester bond were mostly affected by the feed rate. The changes in the AV were also measured at 180 to 200°C at a constant feed rate of water. The AV continued to increase at 160°C, while the AV increased, reached a plateau and then gradually decreased at 180 and 200°C during the late stage of the test period.

Key words: Acid value, Deep frying, Kinetics, Palm oil

1. Introduction

Oils are prone to deterioration by autoxidation at relatively low temperatures and thermal oxidation at high temperatures such as 120 to 180°C. The latter oxidation occurs during deep frying which is widely used in food manufacturing, the food-service industry and home cooking. The deterioration of oil during the frying is inevitable, and causes an unfavorable product smell or color, low digestibility [1] and generation of harmful compounds such as peroxide compounds [2] and acrolein [3, 4]. It would also be of concern regarding the health of consumers and the quality of the final products of the frying process [1, 5].

Materials to be fried usually contain water which would affect the deterioration of the oil [6]. However, little information seems available for the effect of water on the deterioration of the oil during deep frying; especially on kinetics. Knowledge of the kinetics is indispensable for reasonable design of the deep frying operation even if it is empirical. To quantitatively assess the effect, water was added to palm oil, which is one of the oils used widely in food manufacturing, at a constant rate in this study. There are many indications when following the deterioration of oil such as the level of the free fatty acid, color of the oil and polarity of the oil. Among them, we selected an acid value of the oil, which reflects the level of free fatty acid, as a measure of the deterioration.

2. Materials and Methods

2.1 Materials

Palm oil free from tocopherol was supplied by Fuji Oil, Osaka, Japan. The palmitic and stearic acids, and mono- stearyl glycerol were purchased from Nacalai Tesque, Kyoto, Japan. Oleic acid (purity: 90%) and 1,3-dilinoleoyl glycerol were purchased from Sigma, St. Louis, MO, USA. All other chemicals were obtained from either Nacalai Tesque or Wako Pure Chemical Industries, Osaka, Japan.

2.2 Simulated deep-frying

The palm oil (25 g) was placed in a stainless steel test tube (40 mm O.D.). The oil was kept at 180°C, unless otherwise specified, by holding the tube in a heater with an aluminum block (DTU-1C, Taitec, Saitama, Japan). Purified water was fed to the oil through stainless steel tubing (SUS316, 1/16 inch O.D., 1 mm I.D.), which was inserted near the bottom of the test tube at the flow rate of 0 to 0.0482 kg-water/kg-oil/h using a peristaltic pump.
2.3 Determination of acid value

The acid value (AV) was determined by the electrometric titration method [2]. A mixture of isopropanol and toluene (1:1 by vol.) was prepared daily because of their volatility. A 0.01 mol/L KOH ethanolic solution, which was used as the titrant, was prepared as follows: KOH (1.122 g) was dissolved in a minimal volume of water and then filled to 500 mL using ethanol. This solution was also prepared daily and its accurate concentration was determined by titration with 0.01 mol/L hydrochloric acid of a known factor.

An aliquot of the oil was removed with a Pasteur pipette and placed in a glass cup and weighed. The isopropanol/toluene mixture (25 mL) was added to the glass cup to dissolve the oil under magnetic stirring. The solution was titrated with the KOH solution using an F-13 pH meter (Horiba, Kyoto, Japan). The AV in units of mg-KOH/g-oil was calculated as follows:

\[ AV = \frac{(A - B) \times F \times M_{KOH}}{W} \]  

where A and B are the volumes [mL] of the KOH ethanolic solution required for titrating the oil solution and the isopropanol/toluene mixture as a blank, respectively. W is the weight [g] of the sample oil. F is the accurate concentration [mol/L] of the KOH ethanolic solution. \(M_{KOH}\) is the molecular mass of KOH, which is 56.11 g/mol.

2.4 Treatment of fatty acids mixture with or without glycerol

In order to examine whether or not the hydrolysis of palm oil is irreversible, the mixture of constituent fatty acids of palm oil was treated in the presence of glycerol under the conditions where purified water was fed at the flow rate of 0 to 0.046 kg-water/kg-oil/h. Because degradation of the fatty acids was also a concern, the mixture was treated without glycerol. The compositions of the mixtures are shown in Table 1.

The reaction products were analyzed by a TLC-FID (Iatroscan TC-21, Dia-iatron, Tokyo, Japan) with Chromatocoder 21 (System Instruments, Tokyo, Japan). The sample (0.1 g) was dissolved in 10 mL of hexane, a hexane/chloroform mixture (2:1 by vol.) or a chloroform/methanol mixture (2:1 by vol.) depending on the sample solubility in a mixture. The solution (1 μL) was applied to a silica rod (Chromarod-S III, Dia-iatron) and developed with a mixture of benzene, chloroform, diethyl ether and acetic acid (50 : 10 : 5 : 0.7 by vol.). The separated components were detected using an Iatroscan at a scanning speed of 30 s/rod. Retention times for the free fatty acid, monoacyl glycerol, diacyl glycerol, and triacylglycerol were estimated for palmitic acid, monostearyl glycerol, 1,3-dilinoleoyl glycerol, and fresh palm oil, respectively.

3. Results and Discussion

3.1 Change in the acid value for various feed rates of water

Figure 1 shows the transient changes in the AV of palm oil at 180°C and at various feed rates of water. When no water was fed, the AV increased very slowly and reached 0.72 mg-KOH/g-oil at 171 h. However, it rapidly increased when water was fed even at a low rate. Especially, the increase in the AV was significant at

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Table 1 Compositions of fatty acid mixtures with and without glycerol [7].

| Fatty acid mixture with glycerol [% (w/w)] | Fatty acid mixture without glycerol [% (w/w)] |
|------------------------------------------|---------------------------------------------|
| Lauric acid                              | 0.18                                        |
| Myristic acid                            | 0.98                                        |
| Palmitic acid                            | 38.70                                       |
| Stearic acid                             | 4.07                                        |
| Oleic acid                               | 36.78                                       |
| Linoleic acid                            | 8.76                                        |
| Glycerol                                 | 10.53                                       |

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Fig. 1 Changes in the acid value of palm oil at 180°C and at various feed rates of water. The feed rates were (△) 0.89 × 10⁻³, (●) 2.78 × 10⁻³, (●) 5.86 × 10⁻³, (○) 1.84 × 10⁻², and (◇) 4.82 × 10⁻² kg-H₂O/kg-oil/h. The symbol □ indicates that no water was added. The curves were calculated using the estimated rate constants.
feeding rates higher than $3 \times 10^{-3}$ kg-water/kg-oil/h. There was a lag phase in the increase of the AV during the early state. Thereafter, the AV rapidly increased and reached a plateau, and then seemed to gradually decline. The maximum AV was about 20 mg-KOH/g-oil, which was about one tenth of the AV estimated for the complete hydrolysis of the palm oil. This fact indicated the possible reverse hydrolysis between the carboxyl group of the fatty acid and glycerol during the deep frying. The gradual decrease in the AV during the late stage also indicated the decomposition of the fatty acids or AV-positive substances, which will be shown in the next section.

The mixture of fatty acids, the composition of which was almost the same as that of the palm oil, was heated with or without glycerol at 180°C. The change in AV was measured at various feed rates of water (Fig. 2). The mixtures of the fatty acids with or without glycerol were analyzed by the TLC-FID before and after heating for 174 h (Fig. 3). Heat treatment of the mixture without glycerol produced polar compound(s), which corresponds to peak 3 in Fig. 3B. When the mixture with glycerol was heated, many peaks were observed in the TLC-FID chromatograms as well as the peak corresponding to the polar compound(s) (Fig. 3D). Peaks 3 to 5 correspond to the tri-, di- and monoacyl glycerols based on the migration distances of the reagent acyl glycerols during the analysis. These results suggested that the esterification occurred between the fatty acids and glycerol and that the AV at equilibrium for the palm oil would be between 14 and 33 mg-KOH/g-oil. The AV of about 20 mg KOH/g after a prolonged reaction time in Fig. 2 was in this range.

3.2 The kinetic model

Based on the experimental results, the reaction kinetics for describing the change in the AV during batch deep frying was considered. An ester bond in palm oil, E, is reversibly hydrolyzed to an AV-positive compound, A, which would mainly be ascribed to a carboxyl group of the fatty acid and hydroxyl group, H. Compound A is assumed to be irreversibly degraded.

$$E + W \xrightarrow{k_1} A + H$$

$$A \xrightarrow{k_3} \text{[degradation product]}$$

where W represents water, and $k_1$, $k_2$ and $k_3$ are the rate constants.

As will be shown later, the degradation of compound A could be expressed by first-order kinetics. Because there was an induction period in the increase of the AV, it is assumed that compound A acts as a catalyst for the hydrolysis of the ester bond. Although the degradation and polymerization of glycerol may occur at a high temperature, they are not considered due to the lack of sufficient knowledge. Based on these assumptions, the formation rate of compound A is given by Eq. (4).

$$\frac{dm_A}{dt} = k_1 m_E m_W m_A - k_2 m_A m_H - k_3 m_A$$

where $m$ represents the molality. Although Eq. (4) should be described on the basis of the molarities of the
reactants, the molalities were used because the AV is defined as the amount of KOH required for neutralizing the oil of unit weight and because the change in the density of the oil would not be significant during the frying. It is not easy to evaluate the mw, which would reflect the feeding rate of water. Therefore, the product \( k_1 m_w \) is replaced by the apparent rate constant \( k_1' \). Using \( k_1' \), the formation rates of the compound A, the ester bond E and the hydroxyl group H are expressed by Eqs. (5) to (7), respectively.

\[
\begin{align*}
\frac{dm_A}{dt} & = k_1' m_E m_A - k_2 m_A m_H - k_3 m_A \quad (5) \\
\frac{dm_E}{dt} & = k_1' m_E m_A - k_2 m_A m_H \quad (6) \\
\frac{dm_H}{dt} & = k_1' m_E m_A - k_2 m_A m_H \quad (7)
\end{align*}
\]

For the change in the AV for the fatty acid mixture without glycerol, which is shown in Fig. 2, the plots of \( \ln \left( \frac{m_A}{m_{A0}} \right) \) (where \( m_{A0} \) is the initial value of \( m_A \)) versus time lie on a straight line, indicating that the disappearance of compound A obeyed first-order kinetics. The \( k_3 \) value was evaluated from the slope of the line. \( k_1' \) and \( k_2 \) were then determined to fit the experimental results shown in Fig. 1 to the calculated ones by numerically solving Eqs. (5) to (7).

Figure 4 shows the dependencies of the rate constants on the feed rate of water, \( \nu_w \). The rate constant \( k_3 \) scarcely depended on \( \nu_w \). This fact can also be seen from Fig. 2. On the other hand, the rate constants \( k_1' \) and \( k_2 \) were significantly affected by \( \nu_w \), and they remarkably increased when a small amount of water was added. Both \( k_1' \) and \( k_2 \) showed their maximum values at the \( \nu_w \) value of ca. \( 5 \times 10^{-3} \text{ kg-H}_2\text{O/kg-oil/h} \). However, the reason for this phenomenon remains unclear.

### 3.3 Effect of temperature on the AV of palm oil

Figure 5 shows the changes in the AV of palm oil at various temperatures. The \( \nu_w \) was fixed at 0.05 kg-H\(_2\)O/kg-oil/h. At 200°C, the AV increased after a short induction period, and then reached a plateau, the level of which was the lowest at this temperature. The AV similarly increased up to 100 h at 160°C and 180°C. Thereafter, the AV at 180°C leveled off or slightly decline, but that at 160°C continued to increase. These phenomena seemed to be ascribed to the temperature dependence of \( k_3 \). Because the degradation of compound A scarcely proceeded at 160°C due to the low \( k_3 \), the AV continued to increase. At 180°C and 200°C, however, the degradation expressed by Eq. (3) would dominate and the AV gradually decreased after the reaction presented by Eq. (2) almost reached equilibrium.

![Fig. 5](image)

**Fig. 5** Effect of the temperature on the change in the acid value at 0.05 kg-H\(_2\)O/kg-oil/h. The temperatures were (○) 160°C, (△) 180°C and (□) 200°C. The curves were drawn empirically.

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ファーム油を用いた揚げ操作における酸価の変化に対する動力学

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揚げ物は家庭だけでなく食品産業や外食産業で広く行われている操作である。揚げ物は重ね返すと油が劣化し、使用に耐えなくなる。揚げ操作では、材料から持ち込まれる油が揚げ油の劣化に関与していると考えられる。また、揚げ物が吸油して系外に持ち出され油量が減るため、新たな油を追加されることもある。このような複雑な揚げ操作を合理的に実施、制御するには、揚げ油の品質の変化に関する速度論的な知見が必要である。

油の劣化的程度を評価するには、過酸化物価、カルボニル価、色調、粘度などの多くの指標がある。ここでは、アルカリリセロールの加水分解の程度を反映する酸価（acid value；AV）を指標とした。この値は、食品工業において油の劣化的程度を評価する指標として広く用いられている。また同様に、食品工業での利用が多いことから、揚げ油にはファーム油を使用した。

材料から持ち込まれる水の量の影響を定量的に評価するため、所定温度（通常は180℃）に保ったファーム油にポンプを用いて一定流量で水を供給した。適当な間隔で揚げ油の一部を取り出し、電位差滴定法により酸価を測定した。

Fig.1に示すように、水を供給しない場合には、長時間の加熱においても酸価はあまり上昇しなかった。しかし、少しでも水が供給されると酸価は顕著に増加した。水の供給速度が0.003 kg-水/ kg-油/h以上では、とくに酸価の上昇が著しかった。酸価は誘導期を経たのち急激に上昇して最大値に達し、その後徐々に低下する傾向がみられた。酸価の最大値は約20 mg-KOH/g-油であった。この値は、ファーム油が完全に加水分解されたときに示す酸価（計算値）の約1/10であった。このことは、揚げ操作中のファーム油（アルカリリセロール）の加水分解が急激であり、平衡状態に偏移していることを示唆する。

そこで、ファーム油と同様の脂肪酸組成の混合物にグリセロールを加えた場合と加えない場合（Table 1）について酸価の変化を測定した（Fig.2）。グリセロールを添加しなかった場合には、酸価が徐々に減少し、酸価と時間の関係は片対数紙上での直線となった（Fig.2の図）。このことより、脂肪酸（酸価を示す物質）の熱分解は1次反応速度式で表現できことが示された。一方、グリセロールが存在する場合には、酸価は急激に減少し初期値の1/10程度の値に漸近した。また、このときの混合物をTLC-FIDで分析すると（Fig.3）、トリがもとアラキドグリセロールが生成していることが示された。

これらの結果に基づいて、揚げ操作中の酸価の変化を記述する速度式を提出した。ファーム油（アルカリリセロール）中のエステル結合をE、それが加水分解して生成する酸価を示す物質（主として、カルボニル基）と水酸基をそれぞれAとHと表す。酸価の上昇で誘導期が認められたことより、EがAとHに加水分解する過程（式(2))は不可逆であり、分解過程に対してAは自触媒的に作用すると考えた。さらに、Aは1次反応速度式に従って分解して、酸価を示さなくなると考えた。これらの仮定に基づいて、E, AおよびHの変化はそれぞれ式(4), (6)および(7)で与えられる。これらの式は、本来は容量モル濃度に基づいて表記されるべきであるが、酸価が単位重量あたりの油を和算するのに必要なKOH量を定義されること、および揚げ操作中の油の密度の変化は大きくないことより、重量モル濃度で表記した。また、水の濃度mwを正確に求ることは容易ではないので、式(4)の右辺第1項の速度定数k1とmwの積を1つのパラメータk1’として扱い、式(4)を式(5)で表記した。酸価を示す物質Aの分解過程に対する速度定数k1は、グリセロールを添加しない脂肪酸混合物の酸価の変化（Fig.2）より決定した。パラメータk1’とk2はFig.1に示した酸価の経時変化に対応するように決定した。

上記で得られた速度定数k1, k2およびk1’と水供給速度vWの関係をFig.4に示す。k1はvWにあまり依存しなかった。一方、k1’とk2はvWによって大きく影響され、ともにvWが小さい領域でその影響は顕著であった。

また、水の供給速度が一定の条件で、酸価の変化に対する温度の影響を検討した（Fig.5）。160, 180および200℃のいずれの温度においても、誘導期を経たのち急激に酸価が上昇し最大値に達する現象が認められた。酸価の最大値は低温ほど高い値を示し、160℃では酸価がさらに増す傾向が認められた。

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