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Bond reactivity and antioxidant effect on the autoxidation of soybean oil

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ABSTRACT

Soybean oil (SBO) contains many unsaturated fatty acids, so that it can be easily oxidized by air/oxygen. Therefore the autoxidation of soybean oil was performed to investigate the bond reactivities of allylic, bisallylic CH_2, α-CH_2, β-CH_2, chain CH_2 and CH_2O of backbone in the presence and absence of phenolic and aniline antioxidants by means of iodometry and 500 MHz ^{1}H NMR spectroscopy. From the active oxygen concentration, the inhibiting effect and by application of proton integration of each bond of pure and oxidized soybean oil to the first order rate equation, got firstly the orders of the reactivity of each C–H bond and inhibiting effect of antioxidants. In the presence of 2,6-di-*t*-butyl-4-cresol, three phenol adducts from oxidation product also firstly were identified by means of GC–MS spectroscopy.

1. Introduction

Soybean oil (SBO) contains many unsaturated fatty acids while oleic acid has one double bond, linoleic acid two, and linolenic acid three double bonds, so that it can be easily oxidized by air/oxygen which has a triplet electronic configuration at ground state. This oxidation causes rancidity and a decline in quality for food use. To prevent the rancidity of fatty acid esters and fatty triglyceride, tocopherols [1–4] and phenol derivatives [5,9,18] were investigated.

Rancidity (deterioration) of plant oil by the contact with oxygen may go through the following reaction paths [6–8]:

$$RH + O_2 \rightarrow ROOH \quad (1)$$

$$ROOH + RH \rightarrow 2R^{\bullet} + H_2O_2 \quad (2)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \quad (3)$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \quad (4)$$

$$2ROOH \rightarrow ROO^{\bullet} + RO^{\bullet} + H_2O \quad (5)$$

Oxygen molecule existing as a biradical reacts with SBO to form hydroperoxide (Eq. (1)) which reacts further with another SBO forming hydrocarbon free radicals by hydrogen abstraction from SBO (Eq. (2)). According to Eq. (3), SBO free radical readily reacts with oxygen to generate alkyl peroxide radical with low activation energy. This peroxy radical reacts with another SBO producing hydroperoxide (Eq. (4)) which finally dissociates into the peroxy radical, alkoxy radical and water according to Eq. (5). The steps of Eqs. (4) and (5) are the chain propagation steps. If phenolic antioxidant is present in the reaction system, peroxy radical will abstract hydrogen to produce hydroperoxide and phenoxy radical. Reactivity of the phenoxy radical is lower than that of $ROO^{\bullet}$ because of the steric effect of phenol and better stability.

Antioxidant effect of phenolic compounds between structure and oxidation inhibiting effect shows the following relationships [4,5]:

(1) Phenols containing methyl- and *t*-butyl groups which are electron releasing groups show higher oxidation inhibiting effect while the introduction of electron attracting group such as chloro and carbonyl group to a benzene ring decrease the effect.
(2) Steric hindrance of ortho-position to the hydroxyl group greatly affects the radical reaction rate. Reaction rate with radicals increases with smaller steric hindrance while the radical capturing capability against 1 mole of antioxidant decreases [9]. That means the higher steric hindrance to ortho-position restricts the coupling of the same homologs instead of the reaction with one more peroxy radical.
(3) The phenoxy radical produced in Eq. (6) will show higher antioxidant effect with easier delocalizaition of the radical electron.

$$ROO^{\bullet} + PhOH \rightarrow ROOH + PhO^{\bullet} \quad (6)$$

SBO has many different acidic hydrogens such as allylic and bisallylic hydrogen of oleic, linoleic and linolenic fatty acids, and also alpha, beta hydrogen to the carbonyl group as well as consecutive methylene hydrogen in the main chain and backbone and methyl

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hydrogen [10]. These bonds can be oxidized as described from Eqs. (1)–(6). The double bonds present in SBO offer many opportunities to its structure to improve some of the following properties by simple chemical modification. For example, hydrogenation of the double bond producing solid SBO [10] and expoxidation of SBO enabled further modification [11]. Epoxidized soybean oil (ESBO) is commercially available and is widely used as a plasticizer for polyvinyl chloride and tested further as a new biocomposite [11,12]. Structural advantages of SBO and its epoxide are crosslinking with mono- and diamine as well as its double bonds rendering themselves to a modification of double bonds with different bond energy. Main purpose of this work is to investigate the relative reactivity of each bond of pure SBO with or without inhibitors in the autoxidation by means of ^{1}H NMR. Antioxidant effects of phenol derivatives and of aromatic amine on autoxidation were also investigated. Finally the products were identified by IR and GC–MS. Active oxygen during the oxidation was quantified by iodometry. Autoxidation was performed in the absence [13,14] and presence of antioxidants [15]. Antioxidants are interchangeably called inhibitors. They are organic compounds that are added into the organic materials either to retard or inhibit the oxidation of the substrate. They can be classified as a radical trapping or a peroxide decomposing agent [15]. Phenols and secondary aromatic amines used in radical trapping and phosphate used in peroxide decomposing commercially. In this investigation, such radical trapping species were used as phenol derivatives and aromatic amine and the reaction monitored by ^{1}H NMR spectroscopy to quantify the oxidation degree of each bond. Finally the adduct compounds with 2,6-di-*t*-butyl-4-cresol were identified by means of GC–MS.

2. Experimental

2.1. Soybean oil purification [16]

Soybean oil used as a substrate was used after the purification according to the literature [16].

2.2. Autoxidation of SBO [13,14]

2.2.1. Autoxidation of pure soybean oil (SBO)

Into a 200 mL three-necked flask equipped with an oxygen inlet purging tube and a condenser, a magnet bar was put. Then it was set in a silicon oil bath which was equipped with a mechanical stirrer and a thermocoupled heating plate. Into the flask was placed 100 g of purified SBO and heated it up to the set temperature and began to flow the oxygen gas at 1.11 mL/g min through flowmeter as the temperature was raised. In this experiment, pure oxygen was used as oxidizer.

During the oxidation process, 0.5–0.8 g of oxidized SBO was taken in different time intervals and at different temperatures to analyze the active oxygen concentration by iodometry as well as to take ^{1}H NMR.

2.2.2. Autoxidation of SBO in the presence of 1.0 wt% antioxidants

Autoxidation of SBO was carried out in the presence of inhibitor along with 1.0 wt% of substrate. The process was same as that of pure SBO oxidation. In this experiment, 97% 4-butylaniline and 97% phenol, 2,6-dimethylphenol, 2,6-di-*t*-butyl-4-cresol and 4-hydroxy-2,2,6,6-tetramethyl-piperidine-N-oxyl, a stable free radical of HALS, were used as inhibitors.

2.3. Iodometry [17]

Iodometry is a mean of quantification of active oxygen formed during the oxidation. The process of the iodometry employed in this experiment was according to Ref. [17].

2.4. Transesterification of oxidized soybean oil (SBO) [11,16]

The methanolysis of oxidized soybean oil was performed according to Refs. [11] and/or [16].

2.5. ^{1}H NMR spectroscopy

Both DRX-300 FT and 500 MHz Advanced FT-NMR spectrometers (German Brucker) were used with and without internal standard, $CDCl_3$.

2.6. IR spectroscopy

Bio-Rad Digilab Division, FTS-165 FT-IR spectrometer was used.

2.7. GC–MS spectroscopy

Agilen Technologies 6890N Gas Chromayograph/5973N Mass Selective Detector System (Agilen Technologies, USA) was used.

Column: DB-1HT (30 m × 0.25 μm × 0.1 μm)

2.8. Viscosity measurement

An Ubbelhode viscometer (734R) was used to measure the viscosity of the products at 40 °C (ASTM D445-96).

3. Results and discussion

3.1. The autoxidation of soybean oil

The following two figures show the change of concentration of active oxygen during the oxidation of pure SBO and *n*-decane as a comparing substance at 140 °C (Fig. 1) and also at 110, 120 and 130 °C respectively (Fig. 2) and in the presence of inhibitors (Fig. 3). Fig. 1 shows the change of active oxygen concentration of SBO according to the running time at 140 °C. There is no induction period but shows a peak at ca 100 min and a flat line thereafter with decreased active oxygen amount. From this result, the peak could be attributed to the oxidation of labile C–H bonds like allylic, bisallylic and/or alpha hydrogen. Following flat line could be attributed to the oxidation of consecutive methylene hydrogens. This explanation can be supported by the oxidation of *n*-decane which has only eight methylene groups and two methyl groups, under the same conditions at 140 °C with the oxygen flow rate of 1.11 mL/g min as seen in Fig. 1. As shown in Fig. 2, the induction period was appeared and shifted to the longer running time and the active oxygen content increased as the temperature decreased. These phenomena could be explained as the formed SBO

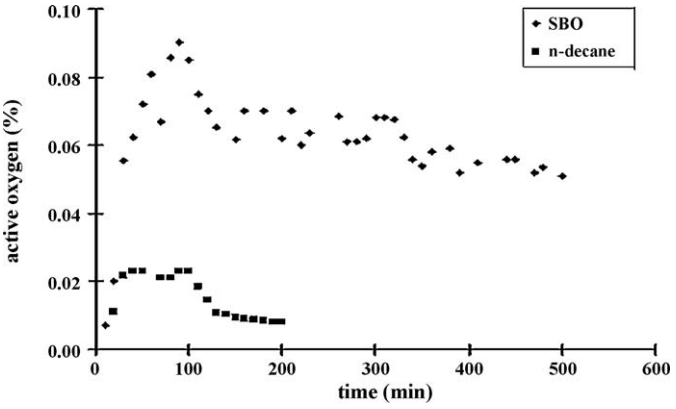

Fig. 1. Change of active oxygen (AO) concentration in the oxidation of SBO and n-decane at 140 °C.