

Effect of Amine-Based Antioxidants as Stabilizers for Biodiesel

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바이오디젤용 산화방지제인 아민안정제들의 효과

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Abstract – Biodiesel is an environmentally-friendly fuel with low smoke emission because it contains about 10% oxygen. Biodiesel fuel prepared by transesterification of vegetable oil or animal fats is susceptible to auto-oxidation. The rate of auto-oxidation depends on the number of methylene double bonds contained within the fatty acid methyl or ethyl ester groups. Biodiesel may be easily oxidized under several conditions, i.e., upon exposure to sunlight, temperature, oxygen environment. Maintenance of the fuel quality of biodiesel requires the development of technologies to increase the resistance of biodiesel to oxidation. Treatment with antioxidants is a promising approach for extending the shelf-life or storage time of biodiesel. The chemical properties of various amine-based antioxidants were evaluated after synthesis of the antioxidants by condensation of phenylenediamine with alkylamines at room temperature. In general, the oxidative stability can be assessed based on various experimental parameters. Such parameters may include temperature, pressure, and the flow rate of air through the samples. The Rancimat method (EN14112) was selected because it is a rapid technique that requires very little sample and provides good precision for oxidative degradation analysis. Specifically, the EN 14112 technique provides enhanced efficiency for oxidative stability evaluation when a larger ester head group is utilized. Therefore, this technique was employed for evaluation of the oxidation stability of biodiesel by the Rancimat method (EN14112).

Keywords – biodiesel(바이오디젤), antioxidant(산화방지제), oxidative stability(산화안정성)

1. Introduction

By definition, biodiesel is derived from transesterification of vegetable oils or animal fats and is composed of saturated and unsaturated long-chain fatty acid esters [1-6]. When exposed to air during storage, autoxidation of biodiesel can cause degradation of the fuel quality. One approach for increasing the resistance

of fatty derivatives to autooxidation is to treat them with oxidation inhibitors, i.e., antioxidants. *p*-Phenylenediamines are useful stabilizers for polymers, particularly as antioxidants and antiozonants for rubbers [7]. They also serve as synthetic starting materials for flavins [8], bis-Troger's bases [9], rod-like oligomers, rotaxanes [10], redox-active macrocycles, and ladder polymers [11-13]. It is known that natural antioxidants, which are often present in the raw materials used for producing biodiesel, are only partially converted to the corresponding esters in concentrations that depend fun-

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damentally on the production technique used [14]. Therefore, depending on the degree of removal of these compounds and especially the degree of unsaturation of the esters produced, the addition of synthetic antioxidants and/or the reintroduction of the natural antioxidants originally present in the starting material can be rather crucial for practical applications [15].

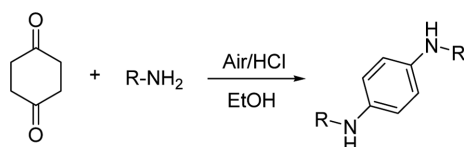
2. Experiments

2-1. Materials and analytical methods

All solvents, reagents, and starting materials were purchased and used without further purification. ^1H NMR spectra were recorded on a Bruker Advance DRX 400 spectrometer at 300 and 500 MHz, respectively. Samples were run in CDCl_3 or $\text{DMSO-}d_6$ and referenced to TMS. The melting points were recorded on a Buchi Melting Point B-544 instrument. GC analyses were carried out using a Hewlett Packard Series 5890 instrument equipped with a SGE BPX5 fused silica column (25 m \times 0.32 mm i.d., 0.5 μm film thickness). The injector and detector temperatures were 250 $^\circ\text{C}$ and 290 $^\circ\text{C}$, respectively. The oven temperature was programmed as follows: initially 50 $^\circ\text{C}$, increase to 290 $^\circ\text{C}$ at 10 $^\circ\text{C min}^{-1}$ and hold for 1 min.

General procedure for synthesis of *N, N'*-dialkyl-*p*-phenylenediamines (DAPD)

A mixture of 1,4-cyclohexanedione (CHD) (0.28 g, 2.5 mmol) and the chosen amine (5.0 mmol) in ethanol was stirred at room temperature while bubbling air through the solution. After completion of the reaction, the solvent was removed under reduced pressure. The residue was dissolved in a minimal amount of acetone, and conc. HCl was added to form the dihydrochloride salt. The product was characterized by ^1H NMR spectroscopy.



Scheme 1. General procedure for synthesis of the antioxidants.

2-2. Experimental methods

Synthesis of *N, N'*-Diethyl-*p*-phenylenediamine (DEPD)

A mixture of 1,4-cyclohexanedione (CHD) (16.8 g, 0.15 mol) and ethylamine (70%, 38.7 g, 0.6 mol) was stirred in ethanol (150 ml) while bubbling air through the solution at room temperature. The reaction was monitored by thin layer chromatography. The solvent in the organic phase was removed under reduced pressure. The separated solid was dissolved in a minimal amount of acetone, and conc. HCl was added to the reaction mixture to generate the dihydrochloride salt (18.6 g, 52.6%). Mass spectral data (EI): found $M = 164$, required $M = 164$, Anal. Calcd. for $\text{C}_{10}\text{H}_{16}\text{N}_2 \cdot 2\text{HCl}$: C, 50.64; H, 7.65; N, 11.81%. Found: C, 50.55; H, 7.52; N, 11.45%. ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ (ppm) 1.22 (t, 6H, $J = 7.22$ Hz), 3.22 (quart, 4H, $J = 7.15$ Hz), 7.46 (s, 4H) 7.80 (s, 2H).

Synthesis of *N, N'*-Dibutyl-*p*-phenylenediamine (DBPD)

A mixture of 1,4-cyclohexanedione (CHD) (16.8 g, 0.15 mol) and butylamine (22.0 g, 0.3 mol) was stirred in ethanol (150 ml) while bubbling air through the solution at room temperature. The reaction was monitored by thin layer chromatography. The solvent was removed from the organic phase under reduced pressure. The separated solid was dissolved in a minimal amount of acetone, and conc. HCl was added to the reaction mixture to generate the dihydrochloride salt (29.0 g, 66.3%). Mass spectral data (EI): found $M = 220$, required $M = 220$, Anal. Calcd for $\text{C}_{14}\text{H}_{24}\text{N}_2 \cdot 2\text{HCl}$: C, 57.34; H, 8.94; N, 9.55%. Found: C, 57.35; H, 8.87; N, 9.31%. ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ (ppm) 0.87 (t, 6H, $J = 7.42$ Hz), 1.34 (multi, 4H, $J = 7.47$ Hz), 1.59 (multi, 4H, $J = 7.9$ Hz), 3.11 (t, 4H, $J = 7.41$ Hz), 7.20 (s, 4H), 7.77 (s, 2H).

Synthesis of *N, N'*-Dihexyl-*p*-phenylenediamine (DHPD)

A mixture of 1,4-cyclohexanedione (CHD) (5.6 g, 0.05 mol) and hexylamine (10.1 g, 0.1 mol) was stirred in ethanol (50 ml) while bubbling air through the solution at room temperature. The reaction was monitored by thin layer chromatography. The solvent was removed from the organic phase under reduced pressure. The separated solid was dissolved in a minimal amount of acetone, and conc. HCl was added to

the reaction mixture to generate the dihydrochloride salt (9.6 g, 55%). Mass spectral data (EI): found $M = 276$, required $M = 276$, Anal. Calcd. for $C_{18}H_{32}N_2 \cdot 2HCl$: C, 62.88; H, 9.81; N, 8.02%. Found: C, 62.23; H, 9.78; N, 7.84%. 1H NMR (300 MHz, DMSO- D_6): δ (ppm) 0.85 (t, 6H, $J = 6.93$ Hz), 1.29 (multi, 12H), 1.59 (multi, 4H, $J = 7.77$ Hz), 3.09 (t, 4H, $J = 7.65$ Hz), 7.14 (s, 4H) 7.88 (s, 2H).

Synthesis of *N,N*-Dioctyl-*p*-phenylenediamine (DOPD)

A mixture of 1,4-cyclohexanedione (CHD) (5.6 g, 0.05 mol) and octylamine (12.9 g, 0.1 mol) was stirred in ethanol (50 ml) while bubbling air through the solution at room temperature. The reaction was monitored by thin layer chromatography. The solvent was removed from the organic phase under reduced pressure. The separated solid was dissolved in a minimal amount of acetone, and conc. HCl was added to the reaction mixture to generate the dihydrochloride salt (14 g, 69.3%). Mass spectral data (EI): found $M = 332$, required $M = 332$, Anal. Calcd. for $C_{22}H_{40}N_2 \cdot 2HCl$: C, 65.16; H, 10.44; N, 6.91%. Found: C, 65.17; H, 10.36; N, 6.72%. 1H NMR (300 MHz, DMSO- D_6): δ (ppm) 0.84 (t, 6H, $J = 6.88$ Hz), 1.23 (multi, 20H), 1.57 (multi, 4H), 3.08 (t, 4H, $J = 7.57$ Hz), 7.14 (s, 4H) 7.92 (s, 2H)

Synthesis of *N,N*-Diphenyl-*p*-phenylenediamine (DPPD)

A mixture of 1,4-cyclohexanedione (CHD) (5.6 g, 0.05 mol) and octylamine (9.3 g, 0.1 mol) was stirred in ethanol (50 ml) while bubbling air through the solution at room temperature. The reaction was monitored by thin layer chromatography. The solvent was removed from the organic phase under reduced pressure. The separated solid was dissolved in a minimal amount of acetone, and conc. HCl was added to the reaction mixture to generate the dihydrochloride salt (7.78 g, 46.9%) Mass spectral data (EI): found $M = 260$, required $M = 260$, Anal. Calcd. for $C_{19}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76%. Found: C, 82.44; H, 6.12; N, 10.70%. 1H NMR (300 MHz, DMSO- D_6): δ (ppm) 6.71 (t, 2H, $J = 7.19$ Hz), 6.95 (d, 4H, $J = 7.89$ Hz), 7.02 (s, 4H), 7.16 (t, 4H, $J = 7.51$ Hz), 7.88 (s, 2H)

Synthesis of *N,N*-Dibenzyl-*p*-phenylenediamine (DBPD)

A mixture of 1,4-cyclohexanedione (CHD) (5.6 g, 0.05 mol) and octylamine (10.7 g, 0.1 mol) was stirred in ethanol (50 ml) while bubbling air through the solution at room temperature. The reaction was monitored by thin layer chromatography. The solvent was removed from the organic phase under reduced pressure. The separated solid was dissolved in a minimal amount of acetone, and conc. HCl was added to the reaction mixture to generate the dihydrochloride salt (10.5 g, 58.4%). Mass spectral data (EI): found $M = 288$, required $M = 288$, Anal. Calcd. for $C_{20}H_{20}N_2 \cdot 2HCl$: C, 66.48; H, 6.14; N, 7.75%. Found: C, 66.45; H, 6.02; N, 7.83%. 1H NMR (300 MHz, DMSO- D_6): δ (ppm) 4.26 (s, 4H), 6.58 (s, 4H), 7.31 (multi, 10H), 7.89 (s, 2H).

Synthesis of *N,N*'-Diphenylethyl-*p*-phenylenediamine (DPEPD)


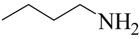
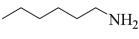
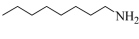
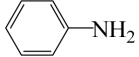
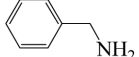
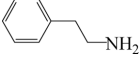
A mixture of 1,4-cyclohexanedione (CHD) (5.6 g, 0.05 mol) and octylamine (24.2 g, 0.2 mol) was stirred in ethanol (50 ml) while bubbling air through the solution at room temperature. The reaction was monitored by thin layer chromatography. The solvent was removed from the organic phase under reduced pressure. The separated solid was dissolved in a minimal amount of acetone, and conc. HCl was added to the reaction mixture to generate the dihydrochloride salt (10 g, 51.7%). Mass spectral data (EI): found $M = 316$, required $M = 316$, Anal. Calcd. for $C_{22}H_{24}N_2 \cdot 2HCl$: C, 67.86; H, 6.73; N, 7.19%. Found: C, 67.83; H, 6.70; N, 7.27%. 1H NMR (300 MHz, DMSO- D_6): δ (ppm) 2.94 (t, 4H, $J = 7.32$ Hz), 3.35 (t, 4H, $J = 8.48$ Hz), 7.24 (multi, 14H) 8.10 (s, 2H).

3. Results and Discussion

3-1. Investigation of synthetic antioxidants

Synthetic routes for developing antioxidants often involve multiple steps, including protection and deprotection that introduce two additional manipulations and lower the atom economy. Further, they employ potentially hazardous alkylation agents or polluting solvents and may generate toxic by-products. The disadvantages include low to moderate yields and the use

Table 1. Yield and reaction conditions for antioxidant preparation

Antioxidant	Reaction material	Reaction temp. (°C)	Yield (%)	Purity (EA,%)	CHD : R-NH ₂
DEPD		rt	52.6%	97%	1:4
DBPD		rt	66.3%	97%	1:2
DHPD		rt	55.0%	97%	1:2
DOPD		rt	69.3%	97%	1:2
DPPD		Reflux	46.9%	99%	1:2
DBPD		rt	58.4%	98%	1:2
DPEPD		rt	51.7%	99%	1:4

a) CHD; cyclohexanedione, b) DEPD; *N,N'*-Diethyl-*p*-phenylene diamine 2HCl, c) DBPD; *N,N'*-Dibutyl-*p*-phenylenediamine 2HCl, d) DHPD; *N,N'*-Dihexyl-*p*-phenylenediamine 2HCl, e) DOPD; *N,N'*-Dioctyl-*p*-phenylenediamine 2HCl, f) DPPD; *N,N'*-Diphenyl-*p*-phenylenediamine 2HCl, g) DBPD; *N,N'*-Dibenzyl-*p*-phenylenediamine 2HCl, h) DPEPD; *N,N'*-Diphenethyl-*p*-phenylenediamine 2HCl

of benzene, which is now considered as an unacceptable solvent due to its carcinogenicity. Therefore, simpler and greener routes are desirable. Leonard and Sauers reported the two-step synthesis of two *N,N,N',N''*-tetraalkyl-*p*-phenylenediamines by condensation of 1,4-cyclohexanedione with secondary amines. This report discloses the first one-step reactions of dione with primary alkylamines in the presence of air for oxidative aromatization at room temperature, without the need for an added catalyst. This method is a convenient and green protocol for synthesis of *N,N'*-dialkyl-*p*-phenylenediamines.

3-2. Effect of antioxidants on the oxidative stability of biodiesel

A Model 743 Rancimat (Metrohm, Herisau, Switzerland) instrument was used to measure the thermal oxidation stability of the fatty acid esters. Over time, oxygen breaks down fats, leading to formation of volatile acids, which affects the consistency and taste of various fatty acid products. The 743 Rancimat accel-

erates this process by exposing the sample to elevated temperatures while pumping air into the sample. The induction time, calculated automatically, is usually a few hours instead of weeks or months, and the time correlates to the shelf life of a product in years. The Rancimat oxidative stability method allows us to test the effectiveness of antioxidants, determine a product's response to antioxidants, determine a product's shelf life, and test the stability of new ingredients. We thus evaluated the effect of the antioxidants on the oxidation stability of biodiesel. The quantity of antioxidant added was varied as 0, 250, 500, and 750 ppm by weight. After determining that the antioxidants were soluble in biodiesel, the test fuels were sampled to examine their oxidation stability. The oxidation stability of the biodiesels was evaluated with a Rancimat 743 (Metrohm Herisau, Switzerland) instrument by applying the accelerated oxidation test specified in EN 14214 [6]. Fig. 2 shows the effect of the antioxidants on the oxidation stability of the biodiesel samples. The efficiency of the antioxidants for promoting the oxida-

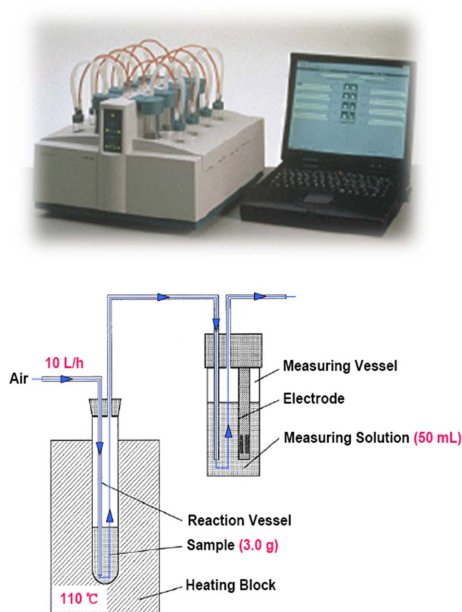


Fig. 1. Schematic of Rancimat 743 instrument used for oxidation test.

Table 2. Oxidation stability of amine-type antioxidants

Antioxidant	BD100	250 ppm/hr	500 ppm/hr	750 ppm/hr
DEPD	3.8	11.4	13.4	14.9
DBPD	3.8	9.1	12.5	13.0
DHPD	3.8	6.3	8.7	11.6
DOPD	3.8	5.1	6.8	8.1
DPPD	3.8	15.3	20.2	23.4
DBPD	3.8	5.3	5.6	7.1
DPEPD	3.8	8.3	10.1	10.5

tion stability of the biodiesel samples evaluated in this study followed the order: Aniline > Et-NH₂ > Bu-NH₂ > He-NH₂ > PEA-NH₂ > Oc-NH₂. Herein, we investigated effect of different antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), tert-butylhydroquinone (TBHQ), propyl gallate (PrG), and α -tocopherol on the oxidative stability of biodiesel samples. The efficiency of the antioxidants for promoting the oxidation stability of biodiesel followed the order: TBHQ > Amine Type > PrG > BHA > BHT > α -tocopherol.

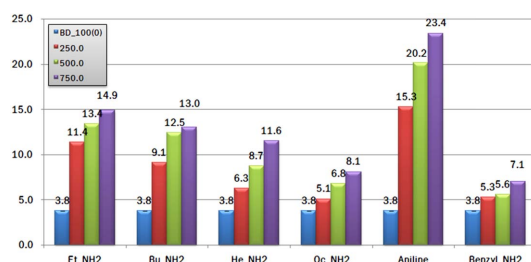


Fig. 2. Stabilizing effects of antioxidants against oxidation of biodiesel. a) Et-NH₂; *N,N*-Diethyl-*p*-phenylenediamine 2HCl (DEPD), b) Bu-NH₂; *N,N*-Dibutyl-*p*-phenylenediamine 2HCl (DBPD), c) He-NH₂; *N,N*-Dihexyl-*p*-phenylenediamine 2HCl (DHPD), d) Oc-NH₂; *N,N*-Dioctyl-*p*-phenylenediamine 2HCl (DOPD), e) Aniline; *N,N*-Diphenyl-*p*-phenylenediamine 2HCl (DPPD), f) Benzyl-NH₂; *N,N*-Dibenzyl-*p*-phenylenediamine 2HCl (DBPD).

4. Conclusions

p-Phenylenediamines were produced by condensation of dione with primary alkylamines in air at room temperature (Table 1). The reactions were conducted in absolute EtOH instead of benzene. Temperatures between ambient temperature and 40 °C were suitable, and air was introduced, preferably by bubbling through the solution. We propose that the synthetic methods presented herein can be used as renewable and sustainable-chemical techniques. Further, this study investigated the effects of antioxidants on the oxidation stability of biodiesel fuels. Among the synthetic antioxidants evaluated, aniline displayed the greatest efficacy for enhancing the oxidation stability in concentrations ranging from 250 to 750 ppm, which qualifies it as a good candidate for use in fuels. The efficiency of the antioxidants investigated in this study followed the order: Aniline > Et-NH₂ > Bu-NH₂ > He-NH₂ > PEA-NH₂ > Oc-NH₂.

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