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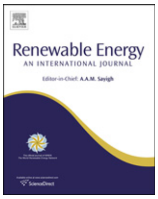

Efficacy of gossypol as an antioxidant additive in biodiesel

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ABSTRACT

The efficacy of gossypol as an antioxidant additive in fatty acid methyl esters (FAMEs) prepared from soybean oil (SME), waste cooking oil (WCME) and technical grade methyl oleate (MO) was investigated. Gossypol is a naturally occurring polyphenolic aldehyde with antioxidant properties isolated from cottonseed that is toxic to humans and animals. At treatment levels of 250 and 500 ppm, gossypol exhibited statistically significant improvements in the induction periods (IPs; EN 14112) of SME, WCME and MO. Efficacy was most pronounced in SME, which was due to its higher concentration of endogenous tocopherols (757 ppm) versus WCME (60 ppm) and MO (0 ppm). A comparison of antioxidant efficacy was made with butylated hydroxytoluene (BHT) and γ-tocopherol. For FAMEs with low concentrations of endogenous tocopherols (WCME and MO), γ-tocopherol exhibited the greatest efficacy, although treatments employing BHT and gossypol also yielded statistically significant improvements to oxidative stability. In summary, gossypol was effective as an exogenous antioxidant for FAMEs investigated herein. In particular, FAMEs containing a comparatively high percentage of endogenous tocopherols were especially suited to gossypol as an antioxidant additive.

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1. Introduction

A principle disadvantage of biodiesel versus petroleum diesel fuel is greater susceptibility to oxidative degradation during storage [1,2]. Oxidative stability is specified in the biodiesel standards ASTM D6751 [3] and EN 14214 [4] (Table 1) and is determined following EN 14112 [5]. The Rancimat method (EN 14112) leverages increased exposure to heat (110 °C) and air (10 L/h) to accelerate oxidative degradation. Oxidation is measured indirectly as the induction period (IP, h) and fuels with longer IPs are more stable to oxidation. Minimum limits for IP of 3 and 6 h are specified in ASTM D6751 and EN 14214, respectively.

The common ground state of oxygen is the diradical triplet state $^3O_2$ and is implicated in autoxidation of lipids. The excited singlet state, $^1O_2$, is 94.2 kJ/mol more reactive and participates in photoxidation [6–8]. Autoxidation initiates at methylene carbons allylic to olefinic moieties along the hydrocarbon tails of biodiesel and consists of initiation, propagation and termination [6–9]. Autoxidation commences with production of resonance-stabilized alkyl radicals by allylic hydrogen abstraction caused by an initiator (Fig. 1). Direct oxidation is spin-forbidden as a result of the opposite spins of $^3O_2$ and lipids in their ground states, thus requiring initiators such as light, heat, peroxides, hydroperoxides and transition metals. Propagation then occurs as a two-step sequence as alkyl radicals react exothermically with $^3O_2$ to produce peroxyl radicals, which in turn react with biodiesel to yield additional alkyl radicals and hydroperoxides (Fig. 1) [6–9]. The conversion of alkyl radicals to peroxyl radicals is comparatively fast whereas transformation to hydroperoxides is rate-limiting. The rate constant for the rate-limiting step of propagation depends primarily on the ease with which a hydrogen atom can be abstracted from the methylene group [6–8]. The bond dissociation energy of an allylic C–H bond (such as in methyl oleate) is approximately 41.9 kJ/mol greater than that of a bis-allylic (such as in methyl linoleate or linolenate) C–H bond [6–9]. Propagation continues so long as there is sufficient supply of reactants. Termination occurs when two radicals react to form stable products, such as aldehydes, shorter-chain fatty acids (FAs), ketones, epoxides, alcohols, dimers, oligomers and polymers, among others [6–9]. The volatile low molecular weight decomposition products are what EN 14112 indirectly measures to determine IP.

Polyunsaturated FA methyl esters (FAMEs) containing one or more bis-allylic methylene positions oxidize quicker than monounsaturated or saturated FAMEs, as seen by the relative rates of

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Abbreviations: AV, acid value; BHT, butylated hydoxytoluene; FA, fatty acid; FAME, fatty acid methyl esters; IP, induction period; IV, iodine value; MO, methyl oleate; PV, peroxide value; RBD, Refined bleached and deodorized; SME, soybean oil methyl esters; WCME, Waste cooking oil methyl esters.

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Table 1
Selected specifications from biodiesel fuel standards ASTM D6751 and EN 14214.

	Units	ASTM D6751	EN 14214
Oxidative stability:			
IP, 110 °C	h	3.0 min	6.0 min
Glycerol content:			
Free	Mass %	0.020 max	0.020 max
Total	Mass %	0.240 max	0.250 max
AV	mg KOH/g	0.50 max	0.50 max
PV	meq/kg	–[a]	–[a]
IV	g I_2/100 g	–[a]	120 max

[a] Not specified.

oxidation of 1, 41, and 98 for ethyl esters of oleic, linoleic and linolenic acids [10]. The IPs of FAMEs from stearic (>40 h), oleic (2.5 h), linoleic (1.0 h) and linolenic (0.2 h) acids further confirm this trend [11]. Methods to improve IP include antioxidants, blending with petrodiesel, reducing exposure to initiators and selection of fuels with fewer polyunsaturated FAs [12–17].

Typical antioxidants include petrochemically-derived synthetics such as tert-butylhydroquinone, butylated hydroxytoluene (BHT) and butylated hydroxyanisole (Fig. 2), among others. Although generally more effective at improving IP than natural antioxidants, synthetics originate from non-renewable materials and may be insoluble at the desired concentration [12,15,18]. Gossypol 2,2′-bis-(Formyl-1,6,7-trihydroxy-5-isopropyl-3-methylnaphthalene; Fig. 3), a polyphenolic aldehyde that possess antioxidant properties, is derived from cottonseed and comprises around 0.1–0.2% of crude cottonseed oil [19–21]. Also found in cottonseed meal, gossypol is toxic to humans and animals. Thus, it must be removed before the oil or meal is used in food applications. In a preliminary study, gossypol delayed oxidation of FAMEs prepared from cottonseed oil [22]. The objective of the current work was to evaluate the efficacy of gossypol in biodiesel prepared from soybean and waste cooking oils, as these are two of the most common feedstocks for biodiesel production in the United States [1].

2. Materials and methods

2.1. Materials

Refined, bleached and deodorized (RBD) soybean oil without additives was purchased from KIC Chemicals, Inc. (New Platz, NY, USA) and used as received. Waste cooking oil methyl esters (WCME) were obtained from Southeast Biodiesel, LLC (North Charleston, SC, USA). FAME standards were purchased from Nu-Chek Prep, Inc. (Elysian, MN, USA). Tocopherol standards (≥97% purity) were obtained from Matreya, LLC (Pleasant Gap, PA). All other chemicals and reagents were purchased from Sigma–Aldrich Corp (St. Louis, MO, USA) and used as received. All measurements were done in triplicate with mean values reported unless otherwise indicated.

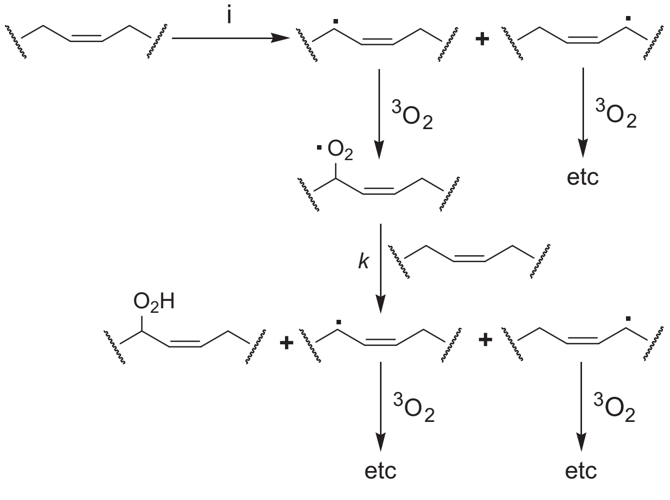

Fig. 1. Simplified pathway of initial lipid autoxidation (i = initiator) by triplet oxygen ($^3O_2$).

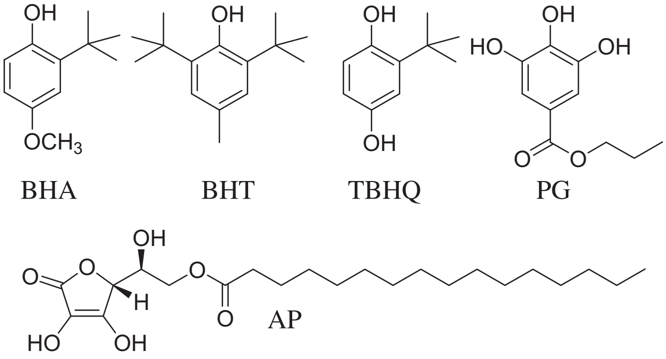

Fig. 2. Chemical structures of the major synthetic antioxidants butylated hydroxyanisole (BHA), BHT, *tert*-butylhydroquinone (TBHQ), propyl gallate (PG) and ascorbyl palmitate (AP).

2.2. Transesterification

Methanolysis of RBD soybean oil was accomplished with sodium methoxide catalyst (0.5 mass % with respect to oil), 6:1 M ratio of methanol to soybean oil and 60 °C internal reaction temperature. After 1.5 h of reaction the mixture was cooled to room temperature. After sequential removal of glycerol by gravity separation and methanol by reduced pressure (10 mbar; 30 °C) rotary evaporation, the crude esters were washed with distilled water until a neutral pH was obtained and dried with $MgSO_4$ to yield soybean oil methyl esters (SME) in high yield (98 mass %).

2.3. Fatty acid profile

FAMEs were separated using a Varian (Walnut Creek, CA, USA) 8400 GC equipped with an FID detector and SP2380 (Supelco, Bellefonte, PA, USA) column (30 m × 0.25 mm i.d., 0.20 μm film

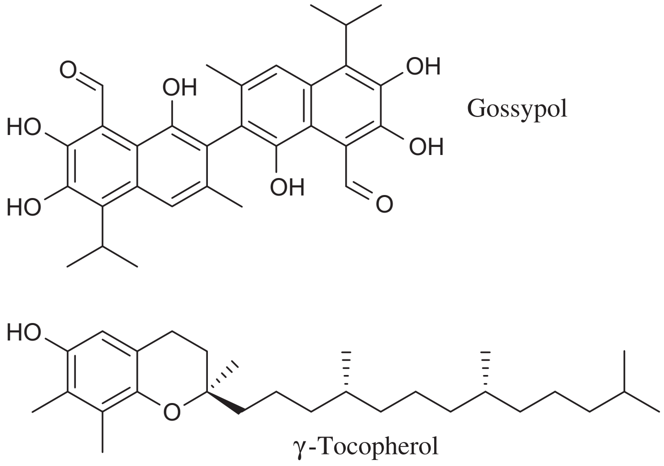

Fig. 3. Chemical structures of the natural antioxidants gossypol and γ-tocopherol.