Effect of Antioxidants on the Oxidative Stability of Biodiesel

Rhet C. de Guzman, Haiying Tang, Steven O. Salley, and K. Y. Simon Ng

Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202

National Biofuels Energy Lab

NEXTENERGY
ECONOMIC SECURITY THROUGH ENERGY DIVERSITY

Introduction

Biodiesel is an alternative fuel composed of saturated and unsaturated methyl ester fatty acids that is very prone to oxidation attack. Exposure to air, heat, light and metallic contaminants can lead to autoxidation, and the degradation of fuel properties such as induction period (IP), kinematic viscosity (ν) and total acid number (TAN). Synthetic antioxidants (AOx) delay the progress of oxidation with varying effectiveness for different biodiesel types. Blending of different AOx could lead to synergisms that provide even grater effectiveness in preventing oxidation.

Objective

- Investigate the effect of different types of AOx in different types of biodiesel
- Elucidate the synergistic effects of synthetic AOx: butylated hydroxyanisole (BHA), propyl gallate (PG), pyrogallol (PY), and t-butyl hydroquinone (TBHQ) in binary formulations in soybean oil- (SBO) and poultry fat- (PF) based biodiesel
- Study the effectiveness of the AOx on the storage stability of biodiesel at long-term storage conditions

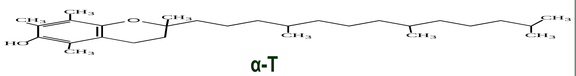
Methods

- Biodiesel: B100 samples of SBO, White grease (WG) (NextDiesel, Adrian, MI); Cotton seed oil (CSO), PF, Yellow grease (YG) (Biodiesel Industries, Denton, TX); and Palm oil (PO) (Biodiesel Board, Malaysia) biodiesel
- Antioxidants: alpha-tocopherol (α-T), Ionol BF200 (IB), BHA, di tert-butyl methylphenol (BHT), di tert-butyl hydroquinone (DTBHQ), TBHQ, PG and PY loaded at various concentrations
- TBHQ blended with BHA, PG and PY at ratios of 1:0, 1:0.33, 1:0.5, 1:1, 1:2, 1:3 and 0:1 (w/w) at 1000 ppm loading
- Stability factor (SF) was computed as:
- Percent synergism (%SYN) was computed using:

$$SF = IP_1 / IP_0$$

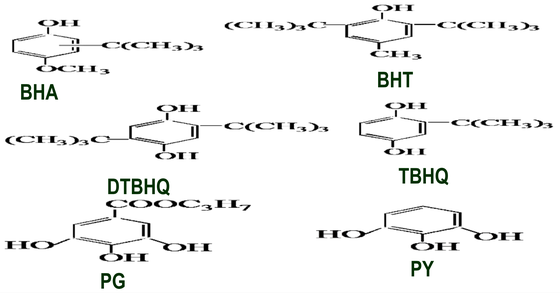
$$\%SYN = \frac{(IP_{mix} - IP_0) - [(IP_1 - IP_0) + (IP_2 - IP_0)]}{[(IP_1 - IP_0) + (IP_2 - IP_0)]} \times 100\%$$

Background: Structures of AOx



α-T

IB: mixture of Mono-, Di-, and Tri- tert-butylphenol



Results: AOx in Different Types of Biodiesel

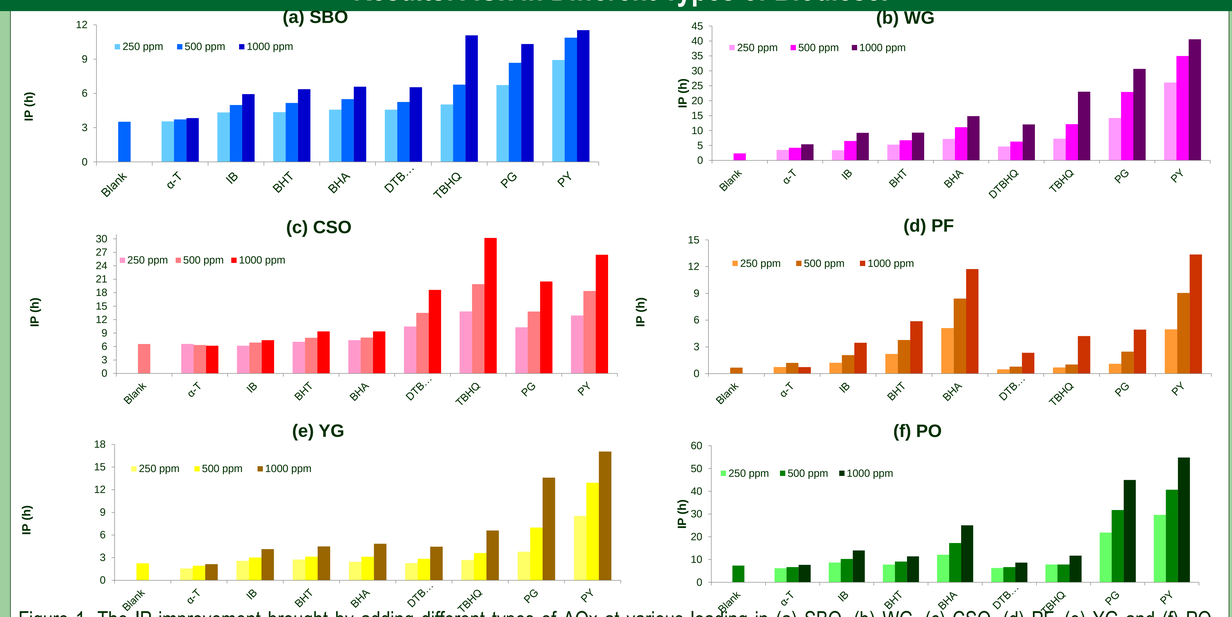


Figure 1. The IP improvement brought by adding different types of AOx at various loading in (a) SBO, (b) WG, (c) CSO, (d) PF, (e) YG and (f) PO. Different types of AOx have different effectiveness with the different types of biodiesel.

Results: Long-term Storage Test

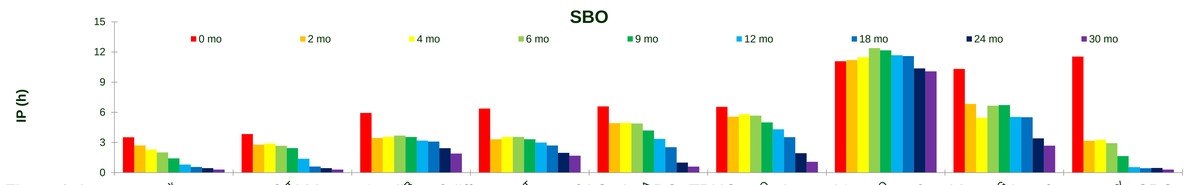


Figure 2. Long-term storage test of 1000 ppm loading of different types of AOx in SBO. TBHQ remains stable even after 30 months of storage in SBO.

Results: Synergistic AOx

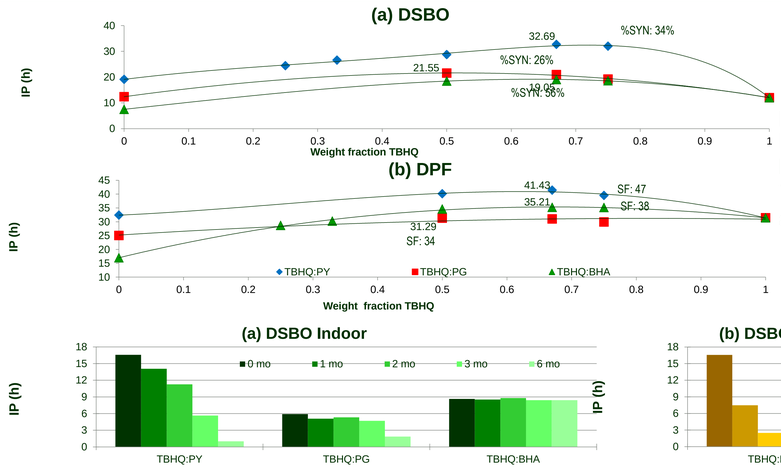
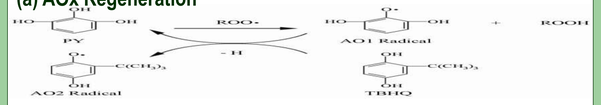


Figure 3. Synergism of binary blends of AOx at 1000 ppm resulting in greatly improved IP of biodiesel: (a) DSBO and (b) DPF. The best combination is gained by using 1:0.5, 1:1 and 1:0.5 for TBHQ:PY, TBHQ:PG and TBHQ:BHA respectively in both (a) and (b).

Figure 3. (a) Indoor and (b) outdoor long-term storage of 500 ppm loading of synergistic AOx blends. TBHQ:BHA is the most stable blend over time.

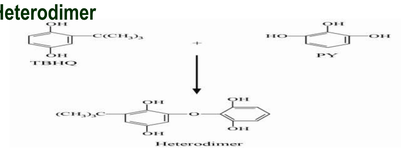
Discussion: Synergistic Mechanism

(a) AOx Regeneration



- Hydrogen is abstracted from active hydroxyl (-OH) groups of one AOx then donated to regenerate the other AOx

(b) AOx Heterodimer



- AOx moieties from the dissociation of parent AOx form heterodimer AOx which have comparable or even better inhibition properties

Figure 4. Proposed mechanisms for the synergistic interaction between TBHQ and PY: (a) AOx regeneration and (b) AOx heterodimer formation.

- The observed AOx synergism is the result of the two proposed mechanisms

Conclusions

- The IP improvement brought by using AOx differ based on the type of biodiesel used. TBHQ, PG and PY have a general effectiveness with the various biodiesel types
- TBHQ gives stable IP improvement after 30 months of long-term storage test. PG and PY effectiveness drop significantly after the first month of storage
- AOx synergy is observed in biodiesel and the best combination is produced by 1:0.5 TBHQ:BHA binary combination in both plant and animal based biodiesel; the combination is also proven to be effective in storage conditions for 6 months
- AOx synergy can have two mechanisms that work together to give improved biodiesel oxidative stability: (1) AOx regeneration and (2) formation of a heterodimer AOx

Future Direction

- Develop robust analytical methods to quantify AOx effectiveness and content
- In-depth study of the AOx synergism mechanism and the molecules produced in the process

Acknowledgement

- Financial support from the Department of Energy (Grant DE-FG36-05GO85005) and the Michigan-Ohio UTC from the USDOT for this research are gratefully acknowledged.

BIODIESEL INDUSTRIES · TARDEC · BOSCH invented for life · DELPHI · CHRYSLER