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Engine Performance Test of Cottonseed Oil Biodiesel

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Abstract: Two cottonseed oil biodiesel samples (cottonseed oil methyl esters, COME) produced in Clemson lab, together with other two commercial cottonseed oil biodiesels were evaluated on their engine performance with the No. 2 diesel fuel as a reference. The results revealed that emission of CO, CO₂ and NO_x from cottonseed oil biodiesels was lower than that of the No. 2 diesel fuel. CO decreased by 13.8%, CO₂ by 11.1% and NO_x by 10%, though there was no significant statistical difference at $p < 0.05$. The engine test also showed a slightly higher amount of consumption and less tendency of coke formation from COME than the No. 2 diesel fuel. The oxidative stability study showed COME with acceptable stability. COME exhibited friendly environmental benefits and acceptable stability, demonstrating its feasibility as an alternative fuel.

Keywords: Biodiesel, cottonseed oil methyl ester (COME), emission, engine performance, oxidative stability, transesterification.

INTRODUCTION

As an alternative and renewable energy source, biodiesel received an increasing interest in recent years because it can reduce global dependence on non-renewable petroleum. Moreover, increased environmental awareness prompts the development of biodiesels with less emission in an effort to reduce the environmental pollution.

In general, biodiesels contain 10% to 11% oxygen by weight, have a higher cetane number than petroleum diesel, have no aromatics, and show some attractive environmental benefits, such as lower emissions of CO, CO₂, and unburned hydrocarbons (HC) [1,2]. Biodiesel is commonly produced through chemical transesterification, a process in which triglycerides in vegetable oils or animal fats react with an alcohol in the presence of a catalyst. The transesterification process results in desirable biodiesel properties such as low viscosity, low molecular weight and high volatility, which overcome common problems such as an incomplete combustion, poor atomization, ring sticking, severe engine deposits, and injector coking that are encountered when natural oils and fats are used [3].

Engine performance test of biodiesels and their blends is indispensable for evaluating biodiesel properties. Several research groups [1, 4] investigated the properties of a biodiesel blend with soybean oil methyl esters in diesel engines and found that particulate matter (PM), CO, and soot mass emissions decreased, while NO_x increased. Labeckas *et al.* [2] examined the performance and exhaust emissions of rapeseed oil methyl esters in direct injection diesel engines, and found that there were lower emissions of CO, carbon dioxide (CO₂) and HC. Similar results were reported [5] for

methyl esters of sunflower oil and olive oil when they were blended with marine diesel and tested in a stationary diesel engine. Raheman *et al.* [6] studied the fuel properties of karanja methyl esters blended with diesel from 20% to 80% by volume. It was found that B20 (a blend of 20% biodiesel and 80% petroleum diesel) and B40 (a blend of 40% biodiesel and 60% petroleum diesel) could be used as appropriate alternative fuels because they had apparently less CO, NO_x emissions, and smoke density. Lin *et al.* [7] confirmed that emission of polycyclic aromatic hydrocarbons (PAH) decreased when the ratio of palm biodiesel increased in a blend with petroleum diesel. In general, biodiesel demonstrated improved emissions by reducing CO, CO₂, HC, PM, and PAH emissions though, in some cases, NO_x increased.

The source of biodiesel usually depends on the crops amenable to the regional climate. In the United States, soybean oil is the most commonly biodiesel feedstock, whereas in Europe, and in tropical countries the rapeseed (canola) oil and palm oil are the most common source for biodiesel, respectively. Cottonseed is a relatively small crop and its oil production volume has been reduced due to the direct feed of whole seed to dairy cattle. Cottonseed oil demonstrated superior lubricity property. Moreover, its unique minor components, such as natural anti-oxidants gossypol [8] and carotene [9] in the oil may play important role in retarding the oil oxidation. Cottonseed oil itself could be a cost-effective component in the formulation to achieve a significant improvement in combustion efficiency, in increasing cetane number and reduction in exhaust in terms of CO, NO_x and PM (unpublished data from Oryxe). Since the properties of biodiesel are in large part correlated with the parent oil, biodiesel produced from cottonseed oil may exhibit appreciable oxidative stability and engine performance.

In this study, two biodiesel products produced from crude cottonseed oil in the Clemson University lab and other two

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commercial cottonseed oil biodiesels were tested on two identical diesel engines located in the Biofuels Engine Testing Laboratory at the University of Georgia in Athens, GA. Their engine performance and emissions were evaluated and compared with the No. 2 diesel fuel. In addition, the effect of pigments on oxidative stability of COME was also examined.

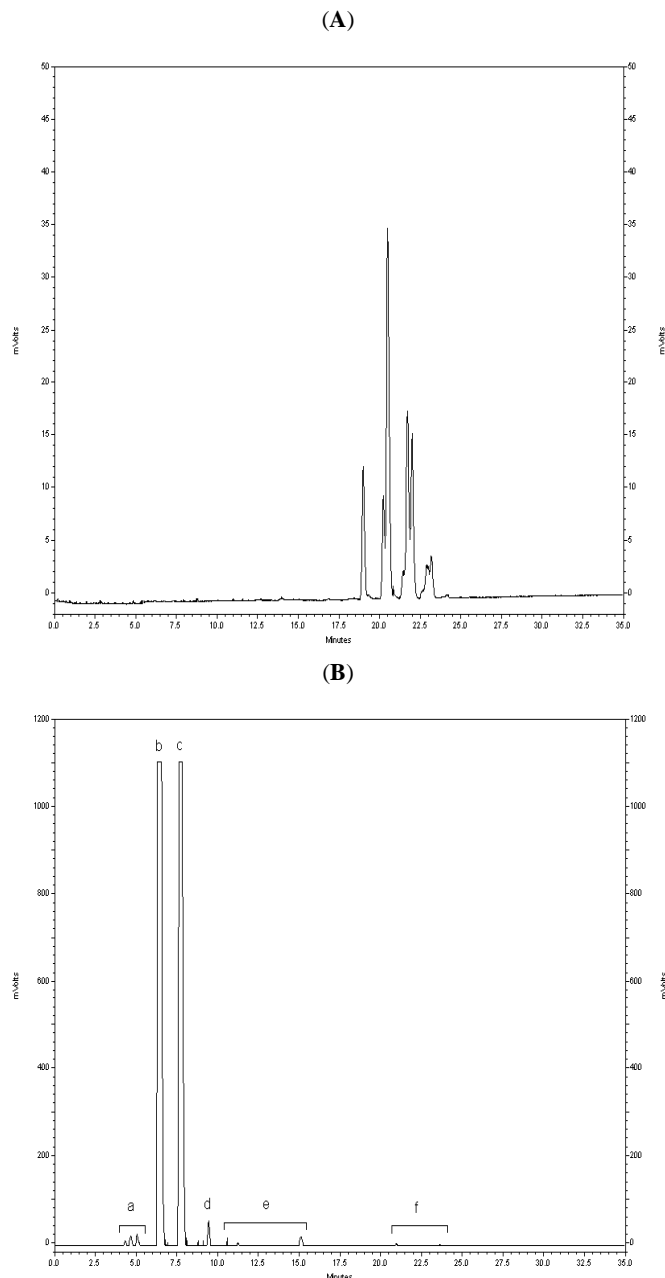


Fig. (1). HPLC chromatogram of crude cottonseed oil (A) and COME (B). Low case letters represent: a: monoglycerides, b: C18-2 (linoleic acid methyl ester), c: C18-1 (oleic acid methyl ester), d: C16-0 (palmitic acid methyl ester), e: diglycerides, f: unreacted triglycerides present in the biodiesel.

MATERIAL AND METHODOLOGY

Fuel Preparation

Cottonseed oil biodiesel COME A and COME B were produced from the same crude cottonseed oil through two

different reaction conditions to prepare COME A with the highest conversion and COME B with the lightest color. Based on the response surface methodology, an optimized transesterification reaction (*i.e.*, temperature at 53°C, catalyst of NaOH at 1.0% based on weight of crude cottonseed oil, methanol/oil molar ratio at 6, and reaction time of 45 min) with conversion of 97% was used to prepare COME A in a temperature-controlled water bath shaker, while COME B was obtained from a non-optimized condition (*i.e.*, temperature at 65°C, catalyst of NaOH at 1.5% based on weight of crude cottonseed oil, methanol/oil molar ratio at 8 and reaction time of 45 min). Briefly, a certain amount of crude cottonseed oil was weighed and added to a fixed Erlenmeyer flask, then a calculated amount of catalyst (sodium hydroxide) dissolved in the required amount of methanol was added. The reaction flask was immersed in the water bath to keep the temperature constant throughout the reaction with defined agitation. The produced COMEs were washed twice at 55°C with 1:1 volume of water. The conversion of the biodiesel from the cottonseed oil (Fig. 1) was quantified by a Shimadzu reverse-phase HPLC connected to an evaporative light scattering detector (ELSD). Phenomenex Gemini C18 column (250×4.6mm, 5µm) was utilized. HPLC grade acetonitrile (A) and dichloromethane (B) were selected as the mobile phase. The gradient program was as follows: Time: (0, 5, 30, 32, 35 min) for solvent B: (0, 15, 70, 70, 0%). The flow rate of the mobile phase was 1.0 ml/min. Twenty microliters of the diluted biodiesel sample was injected *via* autosampler.

All biodiesels, including the COME A and COME B, the commercial Pacific Biodiesel cottonseed oil biodiesel (TX), the PBSY cottonseed oil biodiesel from Safe Renewable (Conroe, TX), the soybean oil biodiesel (SOB) from a Houston-based company, and the No. 2 diesel, were evaluated on engine performance and emissions. Fuel properties and the No. 2 diesel specifications are shown in Table 1 and Table 2, respectively.

Engine Experiments

The protocol used in this study was based on the method of Geller *et al.* with minor modifications [10]. The fuel temperature was maintained at room temperature (20-25°C). The test period was 2 h. Each fuel was tested by two, 6-kW single cylinder, direct injection, water cooled test engines (Kubota model E750). At the end of test, the injectors were carefully removed and transported to the computer vision system. Carbon deposits on injector tips were scanned, while the coke deposits were quantified by using an ImagingSource DMK 21AU04 monochrome digital camera and Image J software [11]. All values were referenced and calibrated to the same clean fuel injector. No. 2 ultra-low sulfur diesel (ULSD) fuel was selected as the baseline reference fuel. A coking index (CI) was assigned to each fuel and was determined using Eq. 1. In this system a coking index <1 indicates less coking than the No.2 diesel and an index >1 indicates more coking than the No.2 diesel.

$$\text{Coking Index (CI)} = \Delta p_{\text{fuel}} / \Delta p_{\text{D2}}, \tag{1}$$

where Δp_i = difference in pixels between image of dirty injector and image of clean injector.

Table 1. Properties of the Commercial Pacific Biodiesel Produced from Cottonseed Oil

Property	Units	ASTM Test Method	Test Results	ASTM D-6751 Specification
Flash point	°C	D-93	218	130 min.
Water and sediment	% volume	D-2079	<0.05	0.05 max.
Carbon residue	% mass	D-4530	0.04	0.05 max.
Sulfated ash	% mass	D-874	0.005	0.02 max.
Kinematic viscosity, 40°C	mm ² /s (CST)	D-445	4.88	1.9-6.0
Cetane number		D-613	49.2	47 min.
Cloud point	°C	D-2500	11	Report value
Copper corrosion		D-130	1A	No. 3 max.
Acid number	mgKOH/g	D-664	0.25	0.80 max.
Free glycerin	% mass	D-6584	<0.01	0.02 max.
Total glycerin	% mass	D-6584	0.09	0.24 max.
Phosphorous content	ppm	D-4951	2.4	10 max.
Sodium	ppm	D-4951	1.3	5 max.
Potassium	ppm	D-4951	0.6	5 max.
Distillation, 90% recovered	°C	D-1160	356	360°C max.

Table 2. Specifications of the No. 2 Diesel

Property	Units	ASTM Test Method	ASTM D-975 Specification
Flash point	°C	D-93	52min.
Water and sediment	% volume	D-2079	0.05 max.
Carbon residue	% mass	D-524	0.35 max.
Kinematic viscosity, 40°C	mm ² /s	D-445	1.9-4.1
Sulfur	% mass	D-2622	0.05 max
Cetane number		D-613	40 min.
Copper corrosion		D-130	No. 3 max.

A fuel consumption index was determined using a similar method shown in Eq. 2 using the total amount of fuel consumed in the Peterson torque test described above.

$$\text{Fuel Consumption Index (FI)} = \frac{\text{Fuel of Interest Consumed}}{\text{ULSD consumed}} \quad (2)$$

With this system an index >1 indicates more consumption than the No.2 diesel and an index <1 indicates less consumption than the No.2 diesel. The ULSD has an index of 1 for both coking and fuel consumption. An ideal fuel has a both coking and fuel consumption indices < 1.

Stack emissions were measured using an ENERAC 3000E. The team recorded both average and instantaneous measurements of exhaust gas concentrations of CO, CO₂, NO_x (NO + NO₂), and sulfur dioxide. The analyzer software program enabled the recording of emission data directly to a spreadsheet file on the hard drive of a laptop computer. The ENERAC 3000 portable emissions analyzer is a self-contained, extractive emission monitoring system utilizing electrochemical sensors with an internal sample pump de-

signed for 600-900 cc/minute. A separate vacuum pump extracted emissions gas from a breaching port and discharged it to the ENERAC. Teflon tubing interconnected a filter probe in the breaching through two moisture condensers to the vacuum pump and then to the analyzer. The ENERAC sensors used an electronically controlled circuit to minimize zero drift and reject cross interference from other compounds, in compliance with EPA Conditional Test Methods (CTM) -022, -030 and -034. Performance specifications of the CTM-022 method are equivalent to US EPA Method 7E requirements. Accuracy of the sensors is +/-2%, and they are capable of operating at 1.5 orders of magnitude of gas concentrations. The tests were done in five replicates for each biodiesel or diesel fuel sample.

Color Measurement and Analyses of Pigments

Color measurement was conducted by using the Minolta Chroma Meter CR-300. Hunter lab color system was selected to record the color difference. In the color L^*a^*b system, L measures the luminous transmission and varies from 100 for perfect transmission to zero for opaque. The a and b

values have no specific numerical limits. Positive *a* value represents redness, while negative *a* for greenness. Similarly, positive *b* is yellowness, while negative *b* for blueness. Pigment, i.e. carotene, was analyzed by RP-HPLC. The Shimadzu HPLC system consisted of photo diode array (PDA) detector with a Phenomenex C18 column (250×4.6mm, 5µm). Mobile phase in an isocratic mode used HPLC grade solvents in a combination of acetonitrile/methanol/dichloromethane in a ratio of 90/8/2 (v/v). The flow rate of the mobile phase was 1.2 ml/min. Twenty microliters of an appropriate diluted sample was injected into the column via an autosampler and monitored by PDA at the wavelength of 450nm during the whole running time of 40min.

Oxidative Stability Measurement

The oxidative stability index was measured according to the AOCS official method Cd 12b-92 at 110°C [12]. The oxidative stability of biodiesel with gossypol addition was evaluated at the gossypol concentrations of 400, 600, 800, and 1000 ppm.

Data Analyses

Statistical analyses were performed by using the SAS program for Windows, Version 9.1, (Cary, NC) to examine the least significant difference (LSD) between the emissions results at the 95% confidence level.

RESULTS AND DISCUSSION

Effect of Feedstocks on Biodiesel Engine Emissions Compared with the No. 2 Diesel

Emission data from the COME (average value for COME A, COME B, commercial Pacific Biodiesel cottonseed oil biodiesel and PPSY cottonseed oil biodiesel), SOB and No. 2 diesel are listed in Table 3.

Table 3. Comparison of Engine Emissions of COME Average, SOB and No. 2 Diesel

	CO (ppm)	CO ₂ (%)	SO _x (ppm)	NO _x (ppm)
COME average	8978 ^a	9.4581 ^a	0 ^a	509.68 ^{a,b}
SOB	10144 ^a	9.328 ^a	0 ^a	448.24 ^b
No.2 diesel	10417 ^a	10.64 ^a	10.5 ^a	567.2 ^a
LSD _{0.05}	4849.8	1.7332	18.273	112.05

Mean values with different superscripts in the same column are significantly different (P< 0.05).

Compared with the No. 2 diesel, COME and SOB had reduced CO emission by 13.8% and 2.6% though there was no significant difference at p<0.05. This reduction might be due to the presence of oxygen in the biodiesel fuel, which enhanced the combustion process [13]. Regarding the CO₂ emission, COME and SOB had 11.1% and 12.3% emission reduction compared with that of the No. 2 diesel. In addition, no SO_x emission was observed in all the vegetable oil biodiesels because neither the COME nor the SOB contained sulfur. Some researches reported that biodiesels had an increased NO_x emission [4,14,15], which was hypothesized that excessive NO_x might be formed in the cylinder where excessive oxygen content in biodiesels facilitated the

oxidization of nitrogen in lean combustion areas. However, in our test the NO_x emission of the COME and SOB exhibited decrease values compared with that of the No. 2 diesel. These findings agree with the result reported by Yücesu *et al.* [16] and Rakopoulos *et al.* [17], who also found that the NO_x emission of biodiesel blends (including COME and SOB) decreased when the percentage of the biodiesel in the blend increased. It was proposed that higher cetane number and the absence of aromatics could, in a large part, offset the possible increase of the NO_x emission caused by the presence of the fuel bound oxygen, and result in a less NO_x production. Lower NO_x emission was also observed on mahua oil methyl ester [13], which was ascribed to the ignition delay that might cause the reduction of peak pressure rise and the decrease of flame temperature because the low pressure and low temperature in the second stage of combustion process could cause the reduction in NO_x emission. In fact, it is generally accepted that the NO_x formation from atmospheric nitrogen is highly dependent upon temperature because high activation energy is needed for the reaction involved. NO_x formation has also been linked to specific engine design. Therefore, the NO_x emission in the biodiesel combustion is dependent not only on the bound oxygen concentration, but also by combustion temperature and time, among which the former may be the most significant factor. Another possibility is that different fuel system designs and engine calibrations may also result in a measurable difference of the NO_x emission from biodiesels. Nevertheless, in our test, the cottonseed oil biodiesel, like the commercial product (i.e., SOB), showed lower emissions of CO, CO₂ and NO_x than those of the No. 2 diesel, which demonstrated the practical and feasible environmental benefits.

Fuel Consumption and Coking

The brake specific fuel consumption (BSFC) is defined as the fuel flow rate divided by the engine’s output power. It has been shown that biodiesels and petrodiesels had the same efficiency in converting the energy in the fuel to power [18]. Therefore, it was reasonable in our observation that the BSFC values of the tested biodiesels (i.e., COME and SOB) were about 12.5% higher than that of the No. 2 diesel (Fig. 2) because the biodiesels had lower energy content, 12.5% less than that of the No. 2 diesel on a weight basis. The Fig. (2) also shows another benefit that both the COME and the SOB demonstrated less engine coking than the No. 2 diesel.

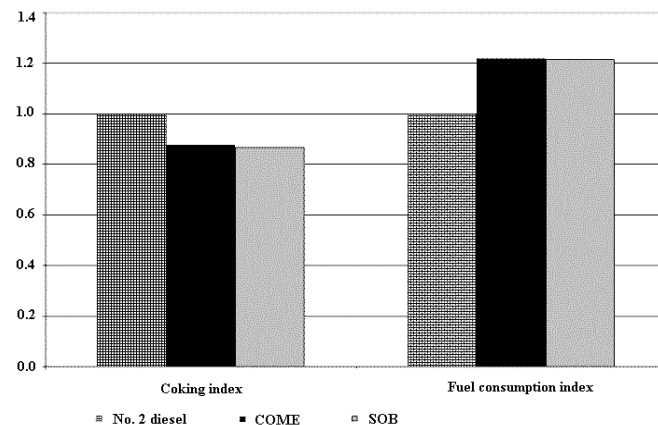


Fig. (2). Fuel consumption and coking index.

Effect of Color (Pigments) in Biodiesel on Oxidative Stability

Biodiesel has many advantages over fossil fuels, but its stability is a big concern, especially when the fuel is produced from fats or oils with high levels of unsaturated fatty acids. Crude cottonseed oil contains approximately 49~58% linoleic acid, which is highly susceptible to oxidation. The antioxidant pigments which cause the color differences in the biodiesels can affect the oxidative stability. Table 4 lists the color difference of all four cottonseed oil biodiesel samples. COME A and COME B had the same fatty acid profiles, but the color of COME B is much lighter than COME A due to less amount of pigments in COME B. From appearance, Pacific Biodiesel cottonseed oil biodiesel had the darkest color, followed by PBSY cottonseed oil biodiesel, COME A, while the COME B had the lightest color.

Table 4. Color Measurement of Biodiesels

	L	a	b
COME A	49.49	-4.90	22.75
COME B	51.86	-2.16	5.04
Pacific biodiesel	37.14	8.23	14.08
PBSY	50.49	-2.91	8.93
SOB	52.13	-1.40	4.91

Table 5 lists the OSI values. All cottonseed oil biodiesels demonstrated acceptable stability according to the ASTM D 6751 specifications that required minimum 3h. In our test, the Pacific Biodiesel possessed the highest OSI value, followed by PBSY, COME A, and COME B. In coincidence, the oxidative stability of biodiesels is correlated to the color appearance of the biodiesels. The darker the biodiesel is, the more stable the biodiesel would be. Therefore, it was hypothesized that some strong antioxidant pigments, such as gossypol and carotene, might have played important roles in stabilizing the biodiesels. Our HPLC analyses confirmed that 2 ppm of carotene and a trace amount of gossypol were present in the COME A, and only a trace amount of carotene and gossypol present in the COME B. This may explain why the COME A was more stable than the COME B. In addition, the Pacific Biodiesel showed the best oxidative stability with the highest carotene content of 8 ppm.

Table 5. Oxidative Stability Comparison of Biodiesels

Sample	Temperature (°C)	Run Time (h)	Method
COME A	110	4.25	All by the AOCs Cd 12b-92
COME B	110	3.00	
Pacific biodiesel	110	11.35	
PBSY	110	10.90	
SOB	110	5.05	

Furthermore, considering the fact that gossypol is a strong antioxidant in cottonseed oil, biodiesel was fortified with gossypol to assess its effect on the OSI value. The

added amount of gossypol in biodiesel was correlated to the oxidative stability of the biodiesel (Table 6). Gossypol exhibited a significant and positive effect on biodiesel stability. For example, an OSI value of 17.2h was achieved for the COME A after 0.1% gossypol was added. Thus, retaining pigments in the biodiesel during production might have positive impact on biodiesel stability.

Table 6. The Effect of Gossypol Addition on COME A's Oxidative Stability

Sample	Gossypol Addition (ppm)	Temp (°C)	OSI (h)	Method
COME A	0	110	4.15	All by the AOCs Cd 12b-92
COME A-4	400	110	5.2	
COME A-6	600	110	6.2	
COME A-8	800	110	8.0	
COME A-10	1000	110	17.2	

CONCLUSIONS

Biodiesel produced from crude cottonseed oil exhibited improved engine performance. Engine test demonstrated that the CO, CO₂, and NO_x emissions all decreased, compared with those of No. 2 ULSD. In addition, the oxidative stability of the cottonseed oil biodiesel was correlated to the content of pigments (such as antioxidants, gossypol, carotene etc.), the darker the color and the more stable the biodiesel, and all the sampled cottonseed oil biodiesel showed acceptable stability according to the ASTM D 6751 requirement.

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