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Utilization of natural compounds (chlorophyll and carotene extracts) as an octane-boosting additive in gasoline

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Abstract. Natural materials should be substituted for organometallic and oxygenated compounds in octane-boosting additives for gasoline because of environmental considerations. Chlorophyll and carotene extracts can be used as octane-boosting additives in gasoline. Maceration and adsorption methods are used to extract them. In this work, chlorophyll and carotene extracts were mixed with fatty acid methyl esters (FAMEs) and a solvent (xylene and gasoline) in a particular composition. The extracted pigment was characterized using ultraviolet–visible (UV–Vis) spectrophotometry. Three different additive formulations with chlorophyll/carotene extract ratios of 0 : 1, 3 : 1, and 2 : 3 were investigated. Additive performance tests included measurements of physical properties, octane number, exhaust hydrocarbon (HC) and carbon monoxide (CO) emissions. The results showed that additives with a chlorophyll/carotene extract ratio of 2 : 3, when added to premium-grade gasoline, increased the octane number by 0.3%. The increase of the octane number was further demonstrated by analysis of the HC composition of the gasoline, where the additive with a 2 : 3 ratio resulted in the greatest increase in the olefin content (22.9%), and the emission tests showed that it could reduce HC emissions by 30.9%.

Keywords: octane boosting additive, gasoline, octane number, chlorophyll and carotene extracts

1. Introduction

The limited ability of refineries to produce gasoline with a high octane number has led to the introduction of octane boosters as gasoline additives into the market. Such fuel additives are a common approach for increasing the octane number of gasoline [1]. The octane number is an important parameter in distinguishing the quality of a fuel [2]. Octane boosters with a considerable improvement effect are generally based on organometallic compounds such as tetraethyl lead (TEL), methylcyclopentadienyl manganese tricarbonyl, and ferrocene. The results of the research showed that TEL is very effective in increasing the octane number of gasoline. However, the use of TEL causes environmental pollution by the lead content of vehicle exhaust emissions. When used as a gasoline additive, TEL may also damage the catalytic converter in the vehicle [3]. TEL is therefore no longer used in gasoline.

Other compounds used as additives to increase the octane number of gasoline include oxygenated compounds such as methyl *tert*-butyl ether (MTBE). This compound can also reduce carbon monoxide

(CO) and NO_x emissions from motor vehicles. However, these compounds are carcinogenic and harmful to human health, and MTBE can contaminate groundwater [4].

In addition to MTBE, oxygenated compounds of the alcoholic groups, such as ethanol, can be used to increase the octane number of gasoline [5]. Their octane-boosting ability is supported by the presence of oxygen atoms that enable fuel to burn more completely; alcohol thus improves combustion efficiency and reduces air pollution [2]. However, the presence of alcohol in fuel can lead to the corrosion of metal components of the fuel system; thus, engines that operate on alcohol-containing fuels must be modified to run on alcohol or run on fuel with a low alcohol concentration [6]. These oxygenated compounds (ethers and alcohols) each have considerable side effects. Thus, the development of natural materials as a source for the manufacture of octane-boosting gasoline additives is needed to enable the production of high-quality fuel with both good engine performance and low environmental impact.

Carotenoid and chlorophyll compounds have been speculated to act as octane boosters in gasoline additives. Carotenoid compounds, as antioxidants, participate in the energy transfer process through electron transfer, thereby protecting the chlorophyll in the main reaction of the combustion process from autooxidation. By contrast, chlorophyll is a complex compound with a high molecular weight, a very high energy content, and an oxygen-rich composition; it thus promotes combustion in the engine's combustion chamber.

The richest natural source of carotenoids is crude palm oil (CPO), in which carotenoids exist primarily as retinol compounds (vitamin A). CPO contains approximately 15–300 times more carotenoid compounds than carrots and is a byproduct of the palm oil industry. Despite its high economic value, CPO has not been optimally utilized [7, 8].

β-Carotene, along with chlorophyll and jojoba oil, has been successfully used as a gasoline additive to enhance combustion characteristics. In this case, carotenoids act as scavengers of pollutants or react with the pollutants present in the fuel [9]. Previous research on carotenoid compounds has been carried out in the energy field, where carotenoid compounds extracted from carrots were used as a combustion-boosting additive in gasoline. The results of the aforementioned study indicate that such additives effectively reduce both CO and hydrocarbon (HC) emissions [10].

In the present study, CPO is used as a source of carotenoids, and *eceng gondok* (water hyacinth, *Eichhornia crassipes*) leaves are used as a source of chlorophyll. CPO was selected because of its high carotenoid content, and water hyacinth was selected as a source of chlorophyll because it is often regarded as a weed or a plant that disrupts the aquatic ecosystem; thus, the development of an application will provide added value to the water hyacinth. In this paper, we report the manufacture of octane-boosting additives for gasoline through the utilization of carotene along with chlorophyll and fatty acid methyl esters (FAMEs) and compare their optimum utilization conditions.

2. Experimental

2.1. Materials and methods

All solvents were used as obtained from commercial suppliers. Isopropanol (IPA), acetone, *n*-hexane, and xylene were of industrial grade (Pro Analysis, PA). Silica gel 60 (0.063–0.2 mm) was used as an adsorbent. Premium gasoline was purchased from the market (a gas station). The water hyacinth leaves (*Eichhornia crassipes*) were acquired from Cipondoh Lake, whereas CPO was acquired from PT Wilmar International Jakarta, rotary evaporator, CFR engine, UV–Vis spectrometer, GC.

2.2. Extraction methods

2.2.1. Chlorophyll extraction. Chlorophyll extraction was carried out by a maceration method from water hyacinth plants. Leaves of water hyacinth were first cleaned and dried. They were then blended until smooth and transferred to a clean container. As much as 500 g of blended water hyacinth leaves was added to 2 L of solvent consisting of a mixture of acetone and hexane (80 : 20, v/v). The maceration process was conducted in dark-colored glass bottles for 24 h in a refrigerator, where the samples were not exposed to direct light. The contents of the bottles were then filtered and concentrated at 40 °C using a vacuum rotary evaporator. The concentration of the extract of chlorophyll obtained was calculated, and it was characterized with an ultraviolet–visible (UV–Vis) spectrophotometer.

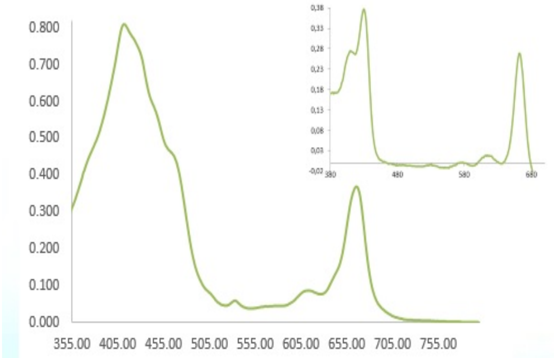

Figure 1. UV–Vis absorption spectra of chlorophyll compared to that of a chlorophyll-*a* standard from Sigma-Aldrich (inset).

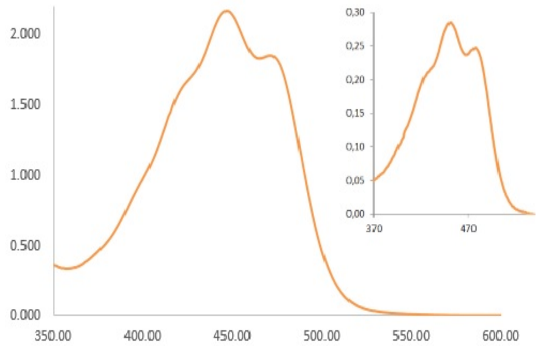

Figure 2. UV–Vis absorption spectra of the carotene extract compared to that of the β-carotene standard from Sigma-Aldrich (inset).

2.2.2. Carotene extraction. Carotene extraction was carried out by adsorption from CPO. 20 g of adsorbent was agitated with an IPA solvent until the adsorbent was submerged. The agitation process was conducted for 15 min at a speed of 1,500 rpm. After the agitation process was completed, the adsorbent was decanted. The CPO was then dissolved in IPA with a ratio of 1 : 3 m/v. Soluble CPO was added to the dried adsorbent, and the IPA was added until the adsorbent was submerged. The adsorption process was carried out at 40 °C for 30 min, and the liquid was then decanted. The adsorbent containing CPO was further extracted with hexane for 3 h and then filtered and concentrated. The concentration of the obtained carotene extract was calculated, and the extract was characterized using UV–Vis spectrophotometry with wavelength range 400–500 nm.

2.3. Manufacture of octane-boosting additives and formulations with gasoline
An octane-boosting additive was made from a mixture of additive A and additive B, which are based on chlorophyll extracts and carotene extracts, respectively. Additives A and B were each added to a FAME and a solvent (xylene and gasoline, respectively) in certain compositions, and they were also mixed with premium-grade gasoline, where the carotene/chlorophyll ratio was 0 : 1, 3 : 1, or 2 : 3. The performance of the additives was investigated by testing the main chemical properties of the gasoline according to the gasoline specifications in Indonesia and by testing the emissions of CO and HCs.

3. Results and discussion

3.1. Chlorophyll and carotene extraction
The percentage yields from the chlorophyll pigment and carotene extraction processes were 23% and 1.4%, respectively.

3.2. Characterization by UV–Vis spectrophotometry
In order to ensure that the extracts obtained were chlorophyll and carotene pigments, characterization was performed by UV–Vis spectrophotometry and the resulting spectra were compared with the absorption spectra of chlorophyll and carotene standards [7]. The spectra show that the extract of chlorophyll exhibits a visible-light absorption spectrum with two main peaks at wavelengths of 413 nm and 666 nm, which is typical for the absorption spectrum of chlorophyll-*a* (figure 1). The spectrum of the carotene extract is similar to that of the β-carotene standard obtained from Sigma-Aldrich (figure 2). The spectrum of the carotene pigment shows three typical absorption peaks in the wavelength region near 400 nm, as observed in both the spectrum of the carotene rough extract CPO and that of the β-carotene standard. The typical peaks in the spectrum of the crude extract of carotene CPO are at wavelengths of 424, 447, and 472 nm.

Table 1: Test results of the main physical and chemical properties of fuel formulations.

Number	Parameter	Gasoline without additive	Gasoline + additive (0 : 1)	Gasoline + additive (3 : 1)	Gasoline + additive (2 : 3)	Specification Limits	
						Min.	Max.
1	Octane number (RON)	88.0	88.0	88.0	88.3	88	-
2	Sulfur content (%wt.)	0.0099	0.0094	0.0102	0.0110	-	0.05
3	Density (kg/m^3)	718.50	719.21	719.41	719.52	715	770
4	Manganase/Iron (mg/L)	0/1.7	0/1.2	0/2.4	0/2.5		
5	Olefine content (%vol.)	13.6115	16.4397	16.7221	17.7964		
6	Aromatic content (%vol.)	6.7023	6.6071	6.7047	6.8610		
7	Wash gum (g/100 mL)	2.4	1.2	1.4	1.6	-	5

3.3. Test results of the main physical and chemical properties

The physical/chemical properties of the gasoline formulations are summarized in table 1. The results of the mercaptan sulfur content analysis showed that the addition of the additive caused a decrease in the mercaptan sulfur value comparable to the concentration of the additive added to premium gasoline. This similarity is attributed to the formation of silver mercaptide at the equivalent point during the analysis. Additives in gasoline affect the formation of silver mercaptide, enabling the equivalent point to be reached faster and lowering the mercaptan sulfur value.

The results of the iron content analysis show that the addition of additives tended to increase the iron content in proportion to the increase in the additive concentration in the premium gasoline. This result is reasonable because the pigment originates from secondary metabolites of plants, where most of the plant cells contain various minerals as nutrients supporting plant metabolism. The presence of iron as an additive will directly improve the performance of the fuel [11].

The results of the gum content analysis gave varying results, although the gum content tended to increase with increasing concentration of the additives in the gasoline. This behavior is strongly influenced by the antioxidant properties of the carotene-pigment components of the additives as well as by the stabilizers of the chlorophyll pigments, which beneficially affect gasoline by decreasing its gum content. This effect is evidenced by the gum content before the addition of additives being higher than that in the premium gasoline after the addition of additives. The gum content is directly proportional to the additive concentration in the premium gasoline [12].

The research octane number (RON) determined by a Cooperative Fuel Research (CFR) engine is useful for stating the fuel's performance and is strongly related to the physical and chemical properties of premium gasoline, which are improved by the addition of chlorophyll and carotene in a 2:3 ratio. The octane number of gasoline is also highly dependent on the composition of its HC compounds, especially its aromatic and olefin contents. Greater aromatic and olefin contents in gasoline lead to higher octane numbers. The test results of the physicochemical properties of the premium gasoline with and without additives showed that no parameter exceeded the maximum limit for gasoline, as specified by the government through the Decree of the Director General of Oil and Gas number 933.K/10/DJM.S/2013 [13].

3.4. Emission testing

Emission testing was carried out on a two-wheeled motor vehicle that was manufactured in 2013. Emission tests were performed under idle machine conditions. The emission test results for premium gasoline with and without additives are shown in table 2.

3.4.1. HC emissions. The successful performance of the chlorophyll and carotene additives is evident from the substantial reductions in HC emission levels. Premium gasoline containing chlorophyll and carotene additives in a 2 : 3 ratio exhibited the best performance. The additives enhanced HC combustion in the machine, resulting in less HC emissions by increasing the combustion heat and

Table 2. Emission test results for premium gasoline under idle machine conditions.

Parameter (ppm)	Premium without additive	Premium + additive A (1 : 0)	Premium + additive B (3 : 1)	Premium + additive C (2 : 3)
Hydrocarbon, HC	259	229	196	180
Carbon monoxide, CO	0.82	1.93	1.55	1.94
Carbon dioxide, CO_2	7.68	6.84	7.41	6.49

maintaining a stable temperature in the test machine [3]. Furthermore, the additive with a 3 : 1 ratio resulted in emissions with the lowest CO content, whereas the additive with a 2 : 3 ratio resulted in emissions with the highest CO content. This increase in CO emissions is derived from the effect of secondary metabolite macromolecules having carbon double bonds and low oxygen content, thereby requiring a high combustion energy and increasing CO emissions [14].

3.4.2. Carbon dioxide (CO_2) emissions. The CO_2 emission for premium gasoline without additives was 7.68 %. Premium gasoline with additive B resulted in CO_2 emissions almost equal to those for premium gasoline without additives. The CO_2 emissions in this case were predominantly unaffected because the ratio of carbon to HC atoms in the fuel was relatively unchanged by the additives. Additives A and C resulted in a slight decrease in CO_2 emission levels. In these cases, the additives also functioned as stabilizers, where the effect of carotene on premium gasoline is more pronounced because these additives have higher concentrations of carotene than chlorophyll. Larger chlorophyll compositions provide more constant combustion, whereas CO_2 emissions are equal to emissions when no additives are used [14]. Emissions of CO_2 from gasoline will increase if there is complete combustion of fuel.

4. Conclusions

From the results presented here, we concluded that the crude extract of carotene from CPO has a visible-light absorption spectrum similar to that of a β-carotene standard, demonstrating that the crude extract contains a carotene pigment. The visible-light absorption spectrum of the chlorophyll extract from water hyacinth leaves is similar to that of chlorophyll-*a*. The blending of these additives with premium gasoline resulted in no substantial change in the physicochemical properties of the gasoline; thus, these gasoline additives can be marketed domestically in accordance with the Standard and Quality of Fuel Type Petrol 88 specified in the Decree of the Director General of Oil and Gas Number 933.K/10/DJM.S/2013 Year 2013. The use of an additive with a chlorophyll/carotene ratio of 2 : 3 in premium gasoline improves the performance of the gasoline compared with the other two investigated additive compositions, especially in terms of increasing the gasoline octane number and decreasing the emissions of HCs. The additive with a chlorophyll/carotene ratio of 2 : 3 can therefore be classified as an octane-boosting additive for gasoline.

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