# Pineapple-stover derived furan compounds as gasoline oxygenate additive

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**ABSTRACT**
Furan compounds have properties such as oxygenate additive to enhance octane number of gasoline. The procedure was a furan synthesis through an acidic hydrolysis of the polysaccharide materials from pineapple plantation residues. The products obtained were a complex mixture of mostly 3-(2-furanyl)-2-propenoic acid, 4-(2-furanyl)-3-butene-2-one and 5-methyl-furfural. Thermodynamic and rheolgical properties of the mixture *in toto* were measured, as well as its oxygenating capability. The results showed a two units enhancer oxygenate additive for naphta, potentially safe for transport and handling, presenting the following characteristics: specific gravity 1,22559±0,00002, kinematic viscosity 0,0127±0,0001 Stokes, enthalpy of vaporization 39,1±0,1kJ $mol^{-1}$, isothermal compressibility (1,0±0.2)$10^{-9}$ $Pa^{-1}$, rate of evaporation 0,03±0,02g $s^{-1}$ $m^{-2}$ and Hildebrand solubility parameter 18,0±0,1(J $cm^{-3})^{1/2}$.

**KEY WORDS**
Pineapple crown, pineapple stubble, research octane number, oxygenate additive, furan compound, methyl terbutyl ether

**RESUMEN**
Los compuestos furánicos tienen propiedades de aditivo oxigenante que les permite incrementar el número de octano de la gasolina. Su síntesis se hizo a través de una hidrólisis ácida de los materiales a base de polisacáridos provenientes de residuos de plantaciones de piña. Los productos obtenidos eran una mezcla compleja, en su mayoría 3 - (2-furanil)-2-propenoico, 4 - (2-furanil)-3-buteno-2-ona y 5-metilfurfural. Se midieron las propiedades termodinámicas y reológicas de la mezcla en su totalidad, así como su capacidad de oxigenación. Los resultados mostraron un aditivo que incrementa en dos unidades el poder oxigenante en la nafta, que es potencialmente seguro para su transporte y manipulación, y que presenta las siguientes características: una gravedad específica de 1,22559±0,00002, una viscosidad cinemática de 0,0127±0,0001 Stokes, una entalpía de vaporización de 39,1±0,1 kJ $mol^{-1}$, una compresibilidad isotérmica de (1,0±0,2)$10^{-9}$ $Pa^{-1}$, una velocidad de evaporación de0,03±0,02g $s^{-1}$ $m^{-2}$y un parámetro de solubilidad de Hildebrand de 18,0±0,1(J $cm^{-3})^{1/2}$.

**PALABRAS CLAVE**
Corona de piña, rastrojos de piña, índice de octano, aditivo oxigenante, compuesto furánico, metil terbutil éter

The finding of alternative energies, fuels and materials is an important goal of current scientific and technological endeavors seeking the break dependence on fossil fuels. One possibility is based on lignocellulosic biomass left from agricultural activities.

Pineapple (*Ananas comosus*) is the second fruit harvest of importance after mango, contributing to over 25 % of the world production of tropical fruits (FAO, 2012)http://faostat.fao.org/DesktopDefault.aspx?PageID=567 - ancor.

In 2010, the principal producing countries were Brazil, Philipines, Costa Rica, Thailand, China, Indonesia and India. Costa Rica contributed 11,3% of the world production (FAO, 2012). Pineapple was the second largest crop of Costa Rica, representing 21% of the national agricultural production (FAO, 2012). Harvesting pineapple generates large amounts of residues such as crown, whole fruits that do not comply with standard quality features and the stubble, that is, the postharvest residue left after 27 months of commercial growth cycle. Crown and stubble amount up to three million tons of residual lignocellulosic biomass every two years (Ramírez, Carazo, Roldán & Villegas, 2007).

This much lignocellulosic biomass could be used as feedstock for the synthesis of an oxygenate additive to act as gasoline octane enhancer.

Oxygenate substances exert their action as octane enhancers due to their greater oxidation degree, compared to hydrocarbons, thus making combustion more rapid and complete, consuming less energy and releasing lesser amount of gases (Speight, 1991). According to the Environmental Protection Agency of the United States of America (EPA), oxygenates must be added in an amount corresponding to 2,0% - 2,7% oxygen content (Klass, 2001). This percentage should increase the research octane number (RON) of gasoline's from 2 to 5 units (Gouli, Lois & Stournas, 1998).

The most used types of oxygenates are alcohols (ethanol and methanol), ethers (methyl tertbutyl ether (MTBE) and ethyl tertbutyl ether) and recently furans compounds synthetized from lignocellulosic biomass. The principal advantage of furan type materials as oxygenants is their relatively high mass content of oxygen per molecule, they can be used in lower concentrations in gasoline to supplement the oxygen percentage set by EPA standards (Huber, Iborra & Corma, 2006). Also, many of these compounds have RON values higher or similar to alcohols and ethers, and reduce the emissions of harmful gases in 7% to 30% (Gouli *et al*., 1998).

## METHODOLOGY

The raw material for the synthesis (pineapple crowns and stubbles) was provided by Pineapple Development Company (Pindeco), from their plantations in Guácimo, Limón, Costa Rica (09°05′20″N, 83°16′07″O). The sample was taken at random with no reposition. Prior to the synthesis, this material was treated as described in the test method TAPPI T-257 cm-02 (TAPPI, 2007)

The synthesis followed the guidelines described by Mascal and Nikitin (2008) with several modifications. The experimental setup used to this purpose was a standard reflux system. It was used 1,000 g – 2,000g of the crown and stubble mixture.

The hydrolysis of polysaccharides was carried out in a reaction flask. The solid pineapple material was mixed with 50mL of water, 37mL of 5g of lithium chloride dissolved in 37mL of concentrated hydrochloric acid and 25 mL of 1,2-dichloroethane. It was heated to reflux at 65°C with continuous mechanical stirring for 18h. A further solution of 2,5g of lithium chloride in 18mL of concentrated hydrochloric acid was added and reflux continued for another 12h.

The organic layer with the reaction product was washed with water to remove residual reagents, distilled to recover the solvent and obtain the reaction product.

Gas-chromatography coupled with mass-spectrometry (GC-MS) was used to identify the products in the reaction mixture. Injecting of 1µL of the raw mixture dissolved in pentane at 250°C using 1/10 split injection, and eluting the sample for 40min with an interface of 35-600m/z at 260°C.

On the reaction mixture, measurements of specific gravity, thermal coefficient of cubic expansion were carried out, and from there, enthalpy of vaporization, Hildebrand solubility parameter and isothermal compressibility were calculated according to the procedure of Castellón-Elizondo, Lutz & Mata-Segreda (2006). The kinematic and dynamic viscosities were determined using the usual procedure described in standards textbooks of experimental physical chemistry, and the rate of vaporization was determined by measuring the weight loss of a specific mass of product contained in a Petri dish as a function of time at 18,9°C. The research octane number was determined with a PetroSpec GS Series Gasoline Analyzers, on mixtures of 7,1 and 10w/v% oxygenate additive (previously dissolved in 10v/v% of toluene) with three fuel materials: composed naphtha, *regular* gasoline and *super* gasoline.

## RESULTS

GC-MS analysis of the product mixture showed the presence of twelve different chemical compounds. It was possible to define the chemical identity of the three most abundant compounds. These compounds were: 3-(2-furanyl)-2-propenoic acid (56,21%), 4-(2-furanyl)-3-buten-2-one (28,67%) and 5-methyl-furfural (6,05%). Their chemical structures are shown in figure 1.

The yield reached in the synthesis was (47,76±0,01)g of furan compounds per 100g of raw plant material.

The results of the physicochemical characterization of the mixture of furan compounds (FM) and MTBE for comparison are shown in Table 1.

Table 2 shows the RON results. FM was dissolved in toluene in order to make RON measurement.

## DISCUSSION

According to the results, the additive synthetized is safer to transport and handle in comparision to MTBE. This is evident from its higher density that gives a lower volume by mass, and its lower thermal coefficient of cubic expansion that controls its expansion when heated. Also, its higher enthalpy of vaporization and lower rate of

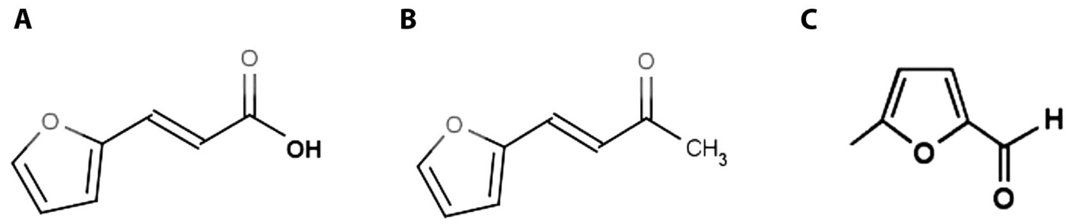


**FIG. 1.** Chemical structures of the major compounds in the mixture of furan compounds obtained.

**TABLE 1**
Physicochemical properties of furans compounds synthesized and methyl tertbutyl ether

| Property | Furan compounds | Methyl tertbutyl ether (Handbook of Chemistry and Physics (2004), Chemexper (2011)) |
|---|---|---|
| Specific gravity at 19,5 °C | 1,22559±0,00002 | 0,7353 |
| Cubic expansion coefficient, $K^{-1}$ | (11,0±0,4)$10^{-4}$ | 14,9$10^{-4}$ |
| Enthalpy ofvaporization, kJ $mol^{-1}$ | 39,1±0,1 | 28,8 |
| Isothermal compressibility, $Pa^{-1}$ | (1,0±0,2)$10^{-9}$ | 2,0$10^{-9}$ |
| Hildebrand solubility parameter, $(J\ cm^{-3})^{1/2}$ | 18,0±0,1 | 14,8 |
| Dynamic viscosity, Poise | 0,0154±0,0001 | 0,0036 |
| Kinematic viscosity, Stokes | 0,0127±0,0001 | 0,0049 |
| Rate of evaporation, g $s^{-1}$ $m^{-2}$ | 0,03±0,02 | 0,0489±0,0006 |
| Relative rate of evaporation (AcOBu = 1)* | 0,62 | 1,01 |

* Calculated in relation to the evaporation of AcOBu = 0,0483±0,0002g $s^{-1}$ $m^{-2}$ (Lutz-Cruz, 2008)

**TABLE 2**
Research octane number and its increment in mixtures of 7,1 and 10,0w/v% furans compounds dissolved in 10,0v/v% of toluene with composed naphtha, regular gasoline and super gasoline

| Sustance | Research octane number | Increment in research octane number |
|---|---|---|
| Composed naphta with 10,0v/v% toluene | 81,1 | 1,6 |
| Composed naphta with 10,0v/v% toluene and 7,1w/v% furans compounds | 82,7 | |
| Composed naphta with 10,0v/v% toluene | 81,1 | 2,4 |
| Composed naphta with 10,0v/v% toluene and 10,0w/v% furans compounds | 83,5 | |
| Regular gasoline with 10,0v/v% toluene | 93,4 | 0,3 |
| Regular gasoline with 10,0v/v% toluene and 10,0w/v% furans compounds | 93,7 | |
| Super gasoline with 10,0v/v% toluene | 96,6 | 0,4 |
| Super gasoline with 10,0v/v% toluene and 10,0w/v% furans compounds | 97,0 | |

vaporization make it less volatile than MTBE, thus generating lower vapor concentrations in the work place.

In regard to its viscosity and isothermal compressibility, it should require of lower pumping work than MTBE for transportation via pipeline.

The Hildebrand solubility parameter of FM is $\delta_H$= 18,00,1(J cm$^{-3}$)$^{1/2}$. It is slightly miscible with naphtas ($\delta_H$= 10,50,2), prediction that is borne out by experiment. This feature poses FM in disadvantage, relative to MTBE. In contrast, FM is soluble in aromatic solvents such as toluene and xylene, that have respectively $\delta_H$ values 18,3(J cm$^{-3}$)$^{1/2}$ and 18,2(J cm$^{-3}$)$^{1/2}$.

The increase achieved on the RON was approximately two units, lower than the increase of four units observed for MTBE at an equivalent oxygen percentage.

FM effect on the RON of *regular* and *super* gasolines was insignificant. (Super gasoline is formulated with 15w/v% of MTBE). The insignificant increment indicates that FM as octane number enhancer is not as strong as oxygenates and octane-boosting substances already present in the gasolines.

However, this is an alternative oxygenate additive to increase the octane number in a few units. For example, to match the increase achieved by MTBE is can be added in twice as much (14 w/v%) and still not be exceeded in quantity MTBE consumption (15w/v%).

FM obtained is an environmentally friendly option as oxygenate additive or as technological solvent material. No matter the use of FM that might be developed in further studies, the utilization of pineapple stover as biorefinery feedstock is an option for the mitigation of the environmental impact of pineapple production.

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