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Design and improvement of biodiesel fuels blends by optimization of their molecular structures and compositions

Felipe A. Perdomo[a,*], *Luis Perdomo*[b], *Beatriz M. Millán*[a], *José L. Aragón*[a]

[a] *Departamento de Nanotecnología, Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Campus Juriquilla, Querétaro, A.P. 1-1010, C.P. 76000, Mexico*

[b] *Departamento de Mecánica y Producción, Universidad Autónoma de Manizales, Manizales, Caldas, Antigua Estación del Ferrocaril, Colombia*

A B S T R A C T

Biodiesel is a renewable alternative to petroleum-based diesel fuel that could potentially still prove to be substantially more environmentally friendly than their fossil alternatives. It is obtained by a transesterification reaction from any triglyceride material (edible and non-edible oils, animal fats, lipid algae, etc.) being a potential tool for sustainable development. Its properties as fuel are strongly linked to the molecular structure of its species composition: profile, chemical structure and quantity of fatty acids alkyl esters contained. Hence the manipulation of this composition could lead to improve different kinds of fuel properties. In this work we implement a group contribution approach of the Statistical Associating Fluid Theory, named SAFT-γ to describe the molecular structure of each fatty ester and to evaluate the influence of its chemical framework in the behavior of biodiesel as fuel by predicting the more relevant thermophysical properties. Parameters for the biodiesel model were obtained by experimental data fitting. Optimal fatty ester composition and potential FAMEs profile were obtained by implementing an Evolutionary Genetic Algorithms (EGA). Biodiesel blends found in this work were compared with two commercial B100 stock in order to analyze its thermodynamical behavior which would be a powerful tool for clean combustion analysis differences.

Keywords: Biodiesel fuel; SAFT-γ; Thermophysical properties; Optimization; Evolutionary Genetic Algorithms

1. Introduction

The accelerated depletion in petroleum sources combined with the high rate of consumption (up to 20 millions Long Tons per day EIA, 2013), has generated the same effect in petroleum reserve and the escalating crude oil prices. Additionally, the excessive use of petroleum-based fuels and its respective environmental damages such as pollution, greenhouse effect and global warming have made renewable fuels an attractive alternative to conventional petroleum-based fuels. In general, biofuels and biomass are now seen as promising and sustainable alternative fuels because of its renewability, better gas emissions and biodegradability. Biomass has been described as the renewable energy source with the highest potential to contribute to the energy needs of modern society (Lynd et al., 1991). Alternative raw materials for biomass based fuels production are triglycerides fats and oils from agro-industrial or extensively grown vegetable sources. Vegetable oils are suitable for diesel fuel owing to their molecular structure (long-chain, saturated, unbranched hydrocarbons) and high energy content which is close to 90% of diesel fuel (Schwab et al., 1987). Direct use of vegetable oils as diesel fuel has not been successful because of its poor properties such as low volatility, reactivity of the unsaturated molecules and high viscosity, which could lead to coking deposition on engine injectors, and plugged orifices during long-time operations of diesel engines (Ali and Hanna, 1994). Transesterification reaction is a common method used to improve fuel properties of

* *Corresponding author*. Tel.: +52 4422381141; fax: +52 4422381165.
E-mail addresses: faperdomoh@fata.unam.mx, feperdomohu@gmail.com (F.A. Perdomo).

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Nomenclature

A	Helmholtz energy
A^{IDEAL}	ideal energy of a chain molecules mixture
A^{MONO}	monomer energy of a chain molecules mixture
A^{CHAIN}	chain energy of a chain molecules mixture
A^{ASSOC}	association energy of a chain molecules mixture
k	Boltzmann's constant
N	molecular numbers
R	gas constant
T	temperature
P	pressure
V	volume
μ	chemical potential
C_v	isochoric heat capacity
C_p	heat capacity at constant pressure
u_s	speed of sound
M_w	molecular weight
ρ	molar density
β_T	isothermal compressibility coefficient
β_s	isentropic compressibility coefficient
$\nu_{k,i}$	number of groups of type k in the molecule i
ν_k^*	number of segments that comprises the k group
σ_{kl}	contact diameter between k and l segments
λ_{kl}	range of the segment–segment SW interaction
ϵ_{kl}	energy depth of the segment–segment interaction
s_k	shape factor of k group
X_{ika}	molecular fraction of species i not bonded at a site of type a, which is located on a type k group
n_{ka}	is the number of associating type a sites in the group k
x_i	molar fraction of i component
w_1,w_2,w_3	weight factors for Eq. (23)
$\vec{X}$	molar fraction vector
T_{bn}	normal boiling point

Subscripts

i, j	component
k, l	group of component i, j
sa	secondary alkanol
aa	alkyl ester
e	proton-accepting type association site
H	proton-donor type association site

Abbreviations

EoS	equation of state
CEoS	cubic equation of state
SAFT	Statistical Associating Fluid Theory
EGA	Evolutionary Genetic Algorithms
FAME	fatty acid methyl esters
H-FAME	hydroxy-fatty acid methyl esters
SW	Square-Well
NG	number of groups
NC	number of compounds
NS	total number of segments
NST_k	number of sites of k type in molecule
YOB	yellow grease oil biodiesel
SOB	soybean oil biodiesel
COB	canola oil biodiesel
TOB	tallow oil biodiesel
MEC18:2	nomenclature for FAMEs (methyl ester with 18 carbon atoms and 2 double bonds)
HB	hydrogen bond
N_p	number of experimental points

vegetable oils and fats. Any triglyceride feedstock present in the vegetable oils and animal fats (include algal lipids) can be transesterified to produce the commonly named biodiesel. It is defined as a oxygenated fuel comprised of monoalkyl esters of long chain fatty acids derived from vegetable oils or animal fats, and is designated by ASTM as B100 (ASTM, 2005). Methanol is the most common alcohol used in the biodiesel production, and therefore it is said that biodiesel is comprised by a mixture of fatty acid methyl esters (FAME). Several fuels quality parameters depend directly upon the fatty acid composition of the biodiesel fuels as cetane number, kinematic viscosity, oxidative stability and cloud point. The most common fatty esters contained in biodiesel are palmitic, stearic, oleic, linoleic and linolenic acids. This holds for biodiesel feedstocks, such as soybean, sunflower, canola, palm and peanut oils (Knothe, 2010). In order to overcome the limitations in the biodiesel production (high manufacturing cost (Ma and Hanna, 1999), suitable flow and combustion properties (Knothe, 2008) and limited availability of feed-stock oil), other non conventional materials like non edible oils (Severino et al., 2012; Agarwal, 2007; Meneghetti et al., 2006, 2007; Mejía et al., 2013) (i.e. Jatropha, karanja, castor oil, etc.) as well as butchery waste and wasted cooking oils (Phan and Phan, 2008), are being worldwide implemented, leading to renewable energy matrix expansion. The biodiesel FAME distribution depends directly on fatty acid profiles presented in the source implemented in the synthesis. Biodiesel molecular structure will vary depending on the feedstocks used for the biodiesel synthesis. Differences in molecular structure (content of different FAME) are highly related to the thermodynamic properties of biodiesel, the physical and chemical processes occurring during the atomization, vaporization and fuel combustion after to be injected into the combustion chamber (Schönborn et al., 2009). Several studies have been oriented to establish a relationship between fuel properties and fatty acid molecular structure and composition (Schönborn et al., 2009; Knothe, 2008; Moser and Vaughn, 2012; Hoekman et al., nd). Similarly, the variability of the biodiesel-derived feedstock will generate differences in biodiesel molecular structure. *These differences lead to distinctive patterns in fuel energy release rates and pollutant formation*. The experimental measure of the aforementioned properties for all possibilities of biodiesel blends fuel types results impractical and expensive. Additionally, The experimental measure of the aforementioned properties for all possibilities of biodiesel fuel blends types results impractical and pretty expensive. Additionally, the experimental data needed to develop thermodynamics models are often limited, specially for complex and large molecules due to experimental measures are extremely costly and time consuming. In so far as, the market starts to accept different biodiesel blends information about physical-chemical properties will become more necessary, thus the development of thermodynamic models is needed to provide an accurate prediction of the physical properties for biodiesel fuels. Several works deal with biofuels thermodynamic properties estimation