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ORIGINAL RESEARCH ARTICLE

Computer-assisted thermochemical study for biodiesel production

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ABSTRACT

The importance of improving industrial transformation processes for more efficient ones is part of the current challenges. Specifically, the development of more efficient processes in the production of biofuels, where the reaction and separation processes can be intensified, is of great interest to reduce the energy consumption associated with the process. In the case of Biodiesel, the process is defined by a chemical reaction and by the components associated to the process, where the thermochemical study seeks to develop calculations for the subsequent understanding of the reaction and purification process. Thus, the analysis of the mixture of the components using the process simulator Aspen Plus V9® unravels the thermochemical study. The UNIFAC-DMD thermodynamic method was used to estimate the binary equilibrium parameters of the reagents using the simulator. The analyzed aspects present the behavior of the components in different temperature conditions, the azeotropic behavior and the determined thermochemical conditions.

Keywords: UNIFAC-DMD; Thermochemistry; Equilibrium; Simulation; Biodiesel

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1. Introduction

Several studies have been developed throughout the world to improve the knowledge of biofuels[1-3], with most of the research directed to the study of chemical combustion, kinetics and behavior of the chemical process[4]. In general, biodiesel production is defined by the chemical reaction of the components, by the technologies and by the catalysts that enhance the process[5].The process intensification (PI) is part of the development of transformation and manufacturing processes, the concept contributes to the reduction of the size of industrial processes, aiming at the integration of processes, modular and compact units[6]. In this work, a thermochemical study of the pure and blended components is developed to understand the phenomenology of biodiesel production.

2. About biodiesel

Biodiesel is defined as a synthetic liquid fuel from a renewable source, its basic composition is a mixture of alkyl esters of long-chain fatty acids obtained from vegetable oils according to the American Society for Testing Materials—ASTM. Generally, biodiesel is obtained from the transesterification reaction, which consists of the reaction of alkanol and triglycerol to form esters and glycerin[7]. The reaction

can be accelerated by acidic, basic, enzymatic or special catalysts[8]. The transesterification process is considered as the most efficient method for the transformation of vegetable oils, because of its practicality and improved properties for use as fuel[9].

Chemical reactions require kinetic data, the kinetics of biodiesel is called as elementary when the order of the reaction coincides with the molecular. The kinetic study of the transesterification reaction has been studied by different research centers, as well as the reaction behavior, oxidation, reaction speed and operating conditions such as temperature[10,11].

Biodiesel is generally obtained from vegetable oils, so it has biodegradable characteristics for more rigorous processes without toxicity. During the conventional production process, the oil is mixed with sodium or potassium hydroxides and an alcohol. The reaction products obtained are Methyl or Ethyl esters (biodiesel) and Glycerol as a by-product[12].

3. Biodiesel characteristics

Currently, the need for alternative fuel substitutes makes biodiesel a great possibility, however, the production of raw material from vegetable oils is not enough, however, there are several justifications for the development of biodiesel processes, among them: the substitution of diesel for biodiesel can be carried out in most diesel-powered equipment, it reduces gas emissions, biodiesel is non-toxic, biodegradable, among others[13]. This need presents a challenge in the balance between agriculture, environment and economic growth. Biodiesel can be obtained by different ways, transesterification or esterification from vegetable oil, a general process project for its production is presented in **Figure 1** and characterized, in sequence, in **Table 1**. The properties and characteristics of biodiesel are presented in **Table 1**.

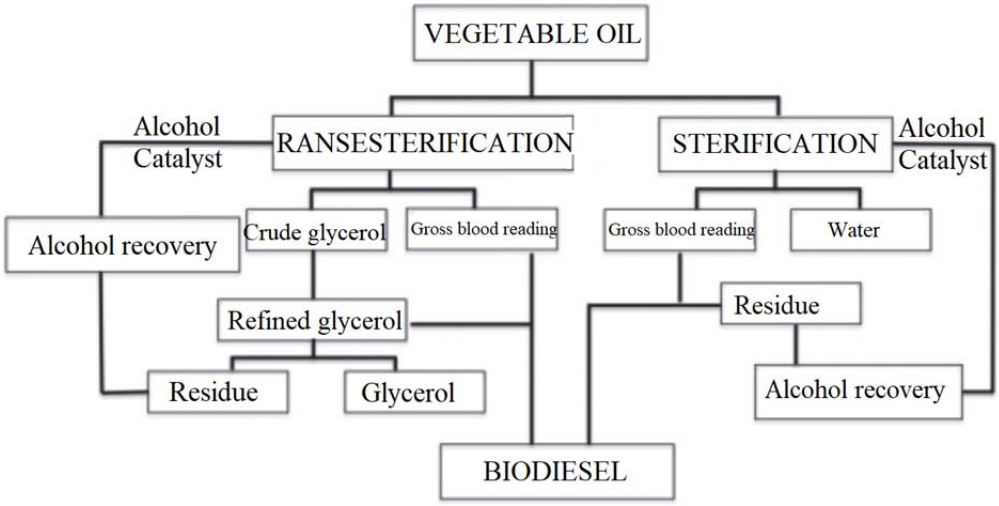

Figure 1. General diagram of biodiesel production from vegetable oil.

Table 1. Biodiesel characteristics

Chemical name	**Fatty acid Methyl ester**
Chemical formula range	C_{14}-C_{24} (m) ethyl ester or $C_{15\text{-}25}H_{28\text{-}48}O_2$
Kinematic viscosity range (mm^2/s at 313 K)	3.3–5.2
Density range (kg/m^3 at 288 K)	860–894
Boiling point range (K)	>475
Interval of the glow point (K)	420–450
Distillation interval (K)	470–600
Vapor pressure (mmHg at 295 K)	<5
Water solubility/physical appearance/ odor/biodegradability/reactivity	Insoluble in water/clear to dark yellow, clear liquid/slightly sugary odor/savory-like/more biodegradable than petroleum diesel/stable, but should avoid contact with strong oxidizing agents

Source: Adapted from Demirbas[13].

Table 2. Technologies for the production of Biodiesel

Variable	Alkaline catalysis	Enzymatic catalysis (Lipase)	Supercritical alcohol	Acid catalysis
Reaction temperature (K)	333–343	303–313	512–658	328–353
Free fatty acids in the PM	Saponified products	Methyl esters	Esters	Esters
Acids in PM	Interferes with the reaction	No influence	-	Interferes with the reaction
Esters Yield	Normal	High	Good	Normal
Glycerol Recovery	Difficult	Easy	-	Difficult
Purification of Methyl esters	Lavagem	None	-	Washing

Note: *PM-Primary Material.

4. UNIFAC-DMD method

Thus, a modification of the base model is the UNIFAC-DMD, this model includes a better prediction of the heat of the mixture, dependence relationship with the temperature and simple parameters for the liquid-vapor and liquid-liquid equilibrium (ELV-ELL). For the development of the calculations, it is sufficient to have information on thermodynamic properties such as: type of mixture, fugacity coefficient, Gibbs energy, enthalpy, entropy and density. In the modification made for the UNIFAC-DMD model, the development of the calculation is significantly different in the combination of the parts, the temperature dependence is described for an equation of interaction of the parameters[14].

Basically the model presents a combinatorial modification when compared to the original UNIFAC[15-17] where the dependence of the temperature on the interaction of the parameters is:

$$ln\,\gamma_i^C = ln\left(\frac{\Phi_i'}{x_i}\right) + 1 - \frac{\Phi_i}{x_i} - \frac{z}{2}q_i\left(ln\frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i}\right) \quad (1)$$

When:

$$\frac{\Phi_i'}{x_i} = \frac{r_i^{3/4}}{\Sigma_j x_j r_j^{3/4}} \quad (2)$$

The dependence is given by the temperature as:

$$\tau_{mn} = e^{-a_{mn}/T} \quad (3)$$

$$a_{mn} = a_{mn,1} + a_{mn,2}T + a_{mn,3}T^2 \quad (4)$$

The parameters used in the simulator are: UFGRPD (k, m, v_m v_k); GMUFDQ (Q_k); GMUFDR-(R_k); UNIFDM/1 (a_{min1}); UNIFDW/2(a_{min2}); UNIFDM/3(a_{min3}).

5. General considerations

The study system involves the following compounds: Methanol (CH_4O), Triolein ($C_{57}H_{104}O_6$), Trimyristin ($C_{45}H_{86}O_6$), Methyl oleate ($C_{19}H_{36}O_2$), Glycerol ($C_3H_8O_3$), NaOH, water, Tripalmitic ($C_{51}H_{98}O_6$) and Methyl Palmitate ($C_{17}H_{34}O_2$-N_1) as main components for biodiesel. Thermodynamic models are of great importance in thermodynamic properties calculations, within the main thermodynamic models found in the Aspen Plus database. It is known that the representation of a system is based on a thermodynamic model and the input data, therefore, the data of the pure components and thermodynamic properties are absolutely necessary to simulate the process. The Aspen Plus V9® process simulator contains the necessary information for the simulation of the system (biodiesel).

The thermodynamic analysis determines the liquid enthalpy deficit and the exegetic losses due to the irreversibility (result of entropy) in each stage of the column. Thus, the study of the unit process from the point perspective, where there is no uniform distribution, deserves improvements. The reduction of the irreversibility allows the increase of the potential work available in the process unit, in proportion, a reduction of the energy consumption and an increase of the efficiency, supported by the concept of a minimum thermodynamic state (MTS).

The methodology adopted for the design of the process is based on obtaining biodiesel in an intensified reaction and separation unit. Thus, the thermodynamic study allows 0 understanding of the phenomena where the biodiesel synthesis occurs.

6. Biodiesel synthesis properties

The properties of the components involved in biodiesel production were estimated in the process simulator and are presented in **Tables 2a** and **2b**.

Table 2a. Properties of the components-BIODIESEL synthesis

Property/Unit	Methanol	OOO	Methyl-O	Glycerol	NaOH	Water	H_3PO_4	Na_3PO_4	Methyl-P
Gibbs standard GI training (J/kmol)	-1.63E + 08	+-2.97E + 8	-1.17E + 08	+-4,47E + 08	+-2,29E + 08	+-2,29E + 08	+-2,29E + 08	+-2,29E + 08	+-2.54E + 08
Standard enthalpy of GI formation (J/kmol)	-2.01E + 08	+-2.02E + 9	-6.26E + 08	+-5.78E + 08	+-2.42E + 08	+-2.42E + 08	+-2.42E + 08	+-2.42E + 08	+-7.01E + 08
Enthalpy of vaporization (J/kmol)	3.53E + 07		6.39E + 07	6.64E + 07	+4.07E + 07	4. 07E+ 07	4.07E + 07	4.07E + 07	5.75E + 07
Standard enthalpy of combustion (J/kmol)	-6.38E + 08	+-3.28E + 10	+-1.11E + 10	+-1.48E + 09	+0	0	0	0	-9.96E + 09
Molecular mass	32.0422	885.449	296.494	92.0947/	-	18.0153	-	-	270.456
Critical pressure (N/m^2)	8.08E + 06	322,432	1.28E + 06	7.50E + 06	+2.21E + 07	2.21E + 07	2. 21E+ 07	2. 21E+ 07	1.24E + 06
Standard specific gravity	0.7962	0.911369	0.872404	1.26124	1	1	1	1	0.869994
Boiling temperature (K)	337.85	813.739	617	561	373.15	373.15	373.15	373.15	597.7
Critical temperature (K)	512.5	943.23	764	850	647.096	647.096	647.096	647.096	762.2
VB (cum/kmol)	0.0427452	2.70798	0.489087	0.08685	0.0188311	0.0188311	0.0188311	0.0188311	0.442809
Critical volume (cum/kmol)	0.117	3.25102	1.06	0.264	0.0559472	0.0559472	0.0559472	0.0559472	1.15
Critical compressibility factor	0.222	0.107	0.214	0.28	0.229	0.229	0.229	0.229	0.224

Table 2b. Properties of the components—BIODIESEL synthesis

Property/Unit	Methyl-M	Methyl-S	1-O	MMM	PPP	PPS	PPO	POS	MMP
Standard heat of formation GI (J/kmol)	-6.44E + 08	+-7. 42E + 08	+-1.16E + 09	+-2.07E + 09	+-2.14E + 09	+-2.18E + 09	+-2.10E + 09	+-2.14E + 09	+-2.09E + 9
Heat of vaporization (J/kmol)	5.44E + 07	6.06E + 07	7.09E + 07	-	-	-	-	-	-
Standard heat of combustion (J/kmol)	-8.81E + 09	+-1.12E + 10	-1.19E + 10	+-	-	-	-	-	-
Molecular weight	242.402	298.51	356.546	723.174	807.336	835.389	833.373	861.427	751.228
Critical pressure (N/m^2)	1.42E + 06	1.08E + 06	1.01E + 06	418.300	366,874	352,837	350,433	337,854	399,391
Standard specific Gravity	0.865421	0.868064	0.953565	0.904398	0.906716	-	-	-	-
Boiling temperature (K)	569.9	623.7	647.017	784.847	794.264	800.847	800.847	807.339	788.187
Critical temperature (K)	741.2	781.1	815.794	898.558	923.368	930.937	930.234	937.526	907.211
Volume score (cum/kmol)	0.993	1.31	1.25028	2.61337	2.94793	3.05945	3.04896	3.16048	2.72489
Compressibility factor review	0.229	0.219	0.204	0.141128	0.197881				

The standard conditions were defined based on experiments reported by the authors under ideal and real conditions in the simulator database. Thus, properties such as molecular mass and critical conditions are taken into consideration to perform the thermochemical study. The transesterification reaction occurs in the presence of alkanol and NaOH catalyst, the excess of alkanol is considered to ensure the production of biodiesel. Considering the development of the conceptual project of the intensified production unit with energy utilization, the separation of fatty acids (Fatty acid methyl ester—FAME) will not be developed, however, the obtaining of FAME will be the main objective to be achieved in the work.

The vapor pressure of the components involved in the biodiesel process describes the behavior of the vapor phase pressure on the liquid phase. It is also studied the dynamic equilibrium that occurs at a certain temperature, in the case of biodiesel, the vapor pressure of the catalysts (Antoine's equation). The parameters for obtaining these variables for each component are presented in **Table 3**.

Table 3. Parameters for estimation of vapor pressure from Antoine Equation

Component	NaOH	H_3PO_4	Na_3PO_4
Temperature	C		
1	-1.00E + 20	-31.5129	-1.00E + 20
2	0	0	-
3	273.15	273.15	273.15
4	0	0	-
5	0	0	-
6	0	0	-
7	0	0	-
8	-273.15	-0.15	-
9	1726.85	199.85	-

To characterize the power equation, the following considerations were taken into account: the equation was described in molar concentration, the exponential temperature factor is considered zero, the characteristics for the pre-exponential factor and activation energy were obtained from the work of Narvaez[18], who presented a proposal of transesterification kinetics for palm oil.

7. Determination of equilibrium parameters

The thermodynamic models evaluated were UNIFAC, UNIFAC-DMD UNIQUAC, NRTL, PENG ROBINSON. Once the properties of the components and the phases present in the operation were studied, the UNIFAC-DMD method was chosen for the synthesis of Biodiesel. This, besides being suggested in the literature, is verified by means of the short analysis method "property method selection" of the Aspen Plus V9® simulator. The UNIFAC-DMD uses the Rendlish-Kwong-Soave state equation, supported by the RK-Soave method, which is calculated by binary equilibrium and determined by the phases with minimum temperature restriction of 290 K (16 °C) and maximum of 420 K (146.85 °C), the method includes higher dependence between the parameters and the temperature and heat of misture[19-21]. The involved components were estimated through the simulator. To facilitate the parameter estimation calculations, the Estimate all missing parameters tool was used for the equilibrium work. The calculations of the physical properties and their behavior in equilibrium were supported by the Rendlich Kwong-Soave model and NRTL for the general treatment with UNIFAC-DMD. The estimated parameters are presented in **Table 4**.

Table 4. Component Properties—TAME Synthesis

Component I	**Methanol**	**Methanol**	**Methanol**	**Methanol**	**Methanol**	**Glycerol**	**Glycerol**	**Glycerol**	**Glycerol**
Component J	Glycerol	NaOH	WATER	H_3PO_4	Na_3PO_4	NaOH	Water	H_3PO_4	Na_3PO_4
Temperature					C				
AIJ	0	-0.693	-0.693	-0.693	-0.693	-0.7318	-0.7318	-0.7318	-0.7318
AJI	0	2.7322	2.7322	2.7322	2.7322	-1.2515	-1.2515	-1.2515	-1.2515
BIJ	547.83	172.987	172.987	172.987	172.987	170.917	170.917	170.917	170.917
BJI	-218.522	-617.269	-617.269	-617.269	-617.269	272.608	272.608	272.608	272.608
CIJ	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
DIJ	0	0	0	0	0	0	0	0	0
EIJ	0	0	0	0	0	0	0	0	0
EJI	0	0	0	0	0	0	0	0	0
FIJ	0	0	0	0	0	0	0	0	0
FJI	0	0	0	0	0	0	0	0	0
TLOWER	25	24.99	24.99	24.99	24.99	25	25	25	25
TUPPER	62.5	100	100	100	100	290	290	290	290

Thermo-physical properties for tri-, di- and mono-glycerides were obtained from the biodiesel database available in the simulator. The study of the system presents an azeotrope at a temperature of 726.45 K (453 °C), a ternary diagram is presented in **Figure 2**, where Glycerol, Methyl-O and Methanol are studied.

The azeotrope has a molar base of 0.4516 and 0.5484 for Glycerol and Methyl-O, respectively.

The thermochemical study developed presents the work plan and behavior of the components for the planning and development of a biodiesel synthesis unit, specifically a reagent unit, aiming at the possibility of obtaining biodiesel and considering limitations in the separation due to the presence of

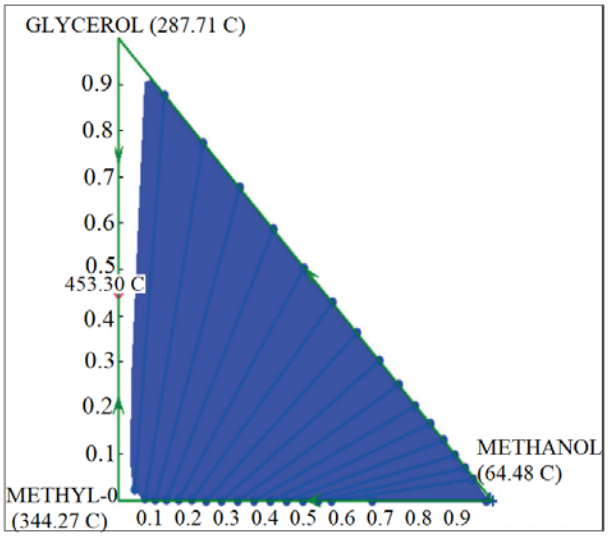

Figure 2. Diagram of Glycerol, Methyl-O and Methanol.

the azeotrope. Glycerol and Methyl-O exhibit azeo-

tropic behavior at 453 OC with a molar composition of 0.4516 and 0.5484, respectively.

8. Conclusions

The particularities of the systems, the azeotropic behavior of the mixtures were identified through the process simulator Aspen Plus V9, taking into account the study of the phenomena and the difficulties of the mixture of components in the production of TAME.

The particularities of the system and the azeotropic behavior were identified for the biodiesel production process. The UNIFAC-DMD method allowed to estimate the equilibrium with precision for the BIODIESEL process. The vapor pressures were fundamental for the phase equilibrium, since the process conditions are a function of the critical points of the components and the temperature at which the azeotropes occur.

It is identified that Glycerol and Methyl-O exhibit azeotropic behavior at 453 OC with a molar composition of 0.4516 and 0.5484, respectively.

Conflict of interest

The authors declared that they have no conflict of interest.

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