Aliphatic acids physical properties evaluation

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ABSTRACT

Biodiesel can be produced from pure fatty acids or from frying oil wastes. To optimize biodiesel manufacturing, many reported studies have built simulation models to quantify the relationship between operating conditions and process performance. For mass and energy balance simulations, it is essential to know the five fundamental thermophysical properties of the feed oil: liquid density (ρ), vapor pressure (P_{vap}), liquid heat capacity (C_p), heat of combustion (ΔH_c) and heat of vaporization (ΔH_{vap}). So, adequate knowledge of physical properties of fatty acids is of great importance for predicting their methyl esters properties which are required to accurately simulate the fuel spray, atomization, combustion and emission formation processes of a diesel engine fueled with biodiesel. In this work a methodology, for predicting liquid density (ρ), liquid heat capacity (C_p), heat of combustion (ΔH_c), heat of vaporization (ΔH_{vap}), liquid viscosity (η), thermal liquid conductivity (λ) and liquid surface tension (σ) of aliphatic acids, is proposed. This methodology will be applied to predict the mentioned above properties for the most of the available fatty acids with focusing an attention on five major fatty acids as they are the main components of oil resources of biodiesel production. These acids are Palmitic acid, Stearic acid, Oleic acid, Linoleic acid and Linolenic acid. For each physical property, the best prediction model has been identified. Some experimental results regarding heat of combustion and heat of vaporization were also obtained. The predicted values were compared with available experimental data and very good agreements have been obtained between the predicted results and the published data where available. The calculated results can be used as key references for biodiesel combustion modeling.

Keywords: Aliphatic acids; Physical properties, Heat of combustion.

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تقدير الخصائص الفيزيائية للحموض الأليفاتية

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الملخص

تتطلب النماذج التمثيلية لتعيين العلاقة الكمية بين شروط التشغيل المثلى ومردود عملية إنتاج البيوديزل، اعتماداً على توازن الطاقة والكتلة، معرفة خمسة مقادير حرارية فيزيائية للزيوت المستخدمة، سواء كانت هذه الزيوت نقية أم نفاية؟، هذه المقادير هي: الكتلة الحجمية للسائل (ρ) وضغط البخار (P_{vap}) والسعة الحرارية للسائل (c_{0})، وحرارة الاحتراق (ΔH_{0})، وحرارة البخر (μ_{vap}). وتكتسب المعرفة الدقيقة بالخصائص الفيزيانية للحموض الدسمة أهمية خاصة عند تقدير خصائص ميتيل إستيرات هذه الحموض اللازمة بدورها لتمثيل عمليات الرش والترذيذ والاحتراق وتشكل الانبعاثات الغازية في محركات الديزل المراودة بالبيوديزل. وبعد أن قُدر ضغط البخار (P_{vap}) سابقاً قام هذا العمل بترتيب أسلوب متكامل لتقدير المرودة بالبيوديزل. وبعد أن قُدر ضغط البخار (P_{vap}) سابقاً قام هذا العمل بترتيب أسلوب متكامل لتقدير الكتلة الحجمية (ρ) والسعة الحرارية (C_p) وحرارة الاحتراق (ΔH_{0}) وحرارة البخر (ΔH_{vap}) واللزوجة المرودة بالبيوديزل. وبعد أن قُدر ضغط البخار (P_{vap}) سابقاً قام هذا العمل بترتيب أسلوب متكامل لتقدير الكتلة الحجمية (ρ) والسعة الحرارية (C_p) وحرارة الاحتراق (ΔH_{0}) وحرارة البخر وحرارة) واللزوجة أدورت المكونات الأساسية لمصادر الزيوت في صناعة البيوديزل. هذه الحموض هي حمض النخل وحمض أدمون الأرية المكونات الأساسية لمصادر الزيوت في صناعة البيوديزل. هذه الحموض هي حمض النخل وحمض أعلاه الطريقة المناسبة لتقديرها، واستكملت بعض النتائج التجريبية المتعلقة بحرارة البخر وحرارة الاحتراق. الشمع وحمض الزيت وحمض الكتان وحمض القنب. وغيّنت اكل خاصة من الخصائص الفيزيائية المذكورة أعلاه الطريقة المناسبة لتقديرها، واستكملت بعض النتائج التجريبية المتعلقة بحرارة البخر وحرارة الاحتراق. أعلاه الطريقة المناسبة لتقديرها، واستكملت بعض النتائج التجريبية المتعلقة بحرارة البخر وحرارة الاحتراق. أعلاه الطريقة المناسبة لتقديرها، واستكملت بعض النتائج التجريبية المتعلقة بحرارة البخر وحرارة الاحتراق. منفع قررنت النتائج التي تم الحصول عليها بالقيم التجريبية المتعلقة، وتبين وجود توافق مقبول مع القيم التجريبية والقيم النظرية المرجعية المنشورة. يمكن استخدام النتائج التي تم الحصول عليها بومغها قيماً مناحياً مناحب

الكلمات المفتاحية: حموض أليفاتية، خصائص فيزيائية، حرارة الاحتراق.

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1. Introduction

Biodiesel fuels derived from vegetable oils or animal fats, which are used as substitutes for conventional petroleum fuel in diesel engines, have recently received increased attention. This interest is based on a number of properties of biodiesel including its biodegradability and the fact that it is produced from a renewable resource [1]. While the high density and viscosity of vegetable oils and animal fats tends to cause problems when used directly in diesel engines, if oils and fats are transesterified using short-chain alcohols, the resulting methyl esters (biodiesel) have viscosities that are closer to petroleum-based diesel fuel. So that the knowledge of their physical properties as a function of temperature and reliable predictive models is of great practical interest for process engineering, considering the demand of computational tools for process design, evaluation, simulation, optimization, control, etc. As biodiesel can directly replace petroleum diesel and be used in diesel engines without the requirement of any major modifications, reducing the country's dependence on imported oil, researchers have shown a growing interest in modeling combustion processes in order to understand the fundamental combustion characteristics of fuels which are renewable, biodegradable and oxygenated such as vegetable oils, their derivative and mixtures. In terms of emissions, researchers have shown that the use of biodiesel can result in a substantial reduction in the unburned hydro-carbon (HC), particulate matter (PM) and carbon monoxide (CO) emissions [2–4], even though a slight increase in nitrogen oxides (NOx) emission is observed [3-6].

To faithfully predict alternative fuel combustion, accurate prediction of the physical properties of alternative fuels is critical in the representation of spray, atomization, and combustion process in the combustion chamber [7]. Lefebvre [8] has proven that physical properties can directly affect combustion performance and CO₂ emissions.

Different models have been developed to predict the properties of biodiesel based on their fatty acid composition [9-11]. However, their predictions are either for a specific fuel, or for a single point of temperature, limiting the usefulness of the information [12-15]. Allen *et al.*, [9,10] predicted the surface tension and viscosity of 15 different biofuels but at a single point of temperature. Yuan *et al.*, [16] presented a method aimed to calculating the physical properties of the biodiesels based on their fatty acid composition over a wide range of temperature, so that it can be used in combustion modeling. However,

the properties were validated for a temperature of up to 373 K, as no published experimental data for higher temperatures were available. Added to the difficulty in obtaining the biofuels physical properties, biodiesel even from the same source may have a different structure and consequently different properties [7].

Atomization quality is influenced by the physical properties of the fuel. Therefore, predicting the physical properties of the vegetables oils and biofuels is a crucial step in the accurate prediction of the spray atomization and combustion processes. Key properties such as vapour pressure, latent heat of vaporization are needed on a temperature range representative of the droplet vaporization and combustion in order to obtain accurate numerical results for combustion modeling.

1.1. The objective goal of the work

The knowledge of physical properties of the main fatty compounds involved in the biodiesel production is essential for process engineering. Although some data have reported properties for some compounds, there is still a necessity for expanding the databank. Hence, the objective of this work is to complete prediction on some physical properties, such as liquid density (ρ), liquid heat capacity (C_p) , heat of combustion (ΔH_c) , heat of vaporization (ΔH_{vap}) , thermal conductivity (λ) and surface tension (σ) of aliphatic acids with focusing attention on five major fatty acids as main components of methyl esters of biodiesel for combustion modeling. These acids are Palmitic acid, Stearic acid, Oleic acid, Linoleic acid and Linolenic acid over a large temperature range. In contrast to traditional methods based on temperature-dependence correlations, methodologies for property prediction based on group contribution methods are presented in this work. Experimental data are gathered from different resourses (see for example [17-21]) as well as obtained using DSC (differential scanning calorimeter) for ΔH_{vap} and bomb calorimeter for ΔH_c .

2. Physical properties prediction models

Table 1 shows the chemical formula, molecular weight and number of atoms of the studied acids. These data will be used for the latter physical properties predictions. For each physical property, various prediction methods are introduced.

Fatty acid name	Chemical	molecular weight	Carbons
Tatty actu hante	structure	[g/mole]	Carbons
formic acid	(CH_2O_2)	46.03	1
Acetic acid	$(C_2H_4O_2)$	60.05	2
Propinionic acid	$(C_{3}H_{6}O_{2})$	74.08	3
Butyric	$(C_4H_8O_2)$	88.11	4
valeric	$(C_5H_{10}O_2)$	102.13	5
Caproic	$(C_6H_{12}O_2)$	116.16	6
Enanthic	$(C_7H_{14}O_2)$	130.18	7
Caprylic	$(C_8H_{16}O_2)$	144.21	8
Pelargonic	$(C_9H_{18}O_2)$	158.23	9
Capric	$(C_{10}H_{20}O_2)$	172.26	10
Lauric	$(C_{12}H_{24}O_2)$	200.31776	12
Myristic	$(C_{14}H_{28}O_2)$	228.37092	14
Palmitic	$(C_{16}H_{32}O_2)$	256.42	16
Stearic	$(C_{18}H_{36}O_2)$	284.48	18
Arachidic	$(C_{20}H_{40}O_2)$	312.53	20
Behenic	$(C_{22}H_{44}O_2)$	340.58	22
Lignoceric	$(C_{24}H_{48}O_2)$	368.63	24
<u>Cerotic</u>	$(C_{26}H_{52}O_2)$	396.69	26
Myristoleic	$(C_{14}H_{26}O_2)$	226.36	14
Palmitoleic	$(C_{16}H_{30}O_2$	254.408	16
<u>Sapienic</u>	$(C_{26}H_{30}O_2)$	254.41	16
<u>Oleic</u>	$(C_{18}H_{34}O_2)$	282.46	18
Vaccenic	$(C_{18}H_{29}O_2)$	282.461	18
Elaidic	$(C_{18}H_{34}O_2)$	282.46	18
Erucic	$(C_{22}H_{42}O_2)$	338.57	22
Nirvonic	$(C_{24}H_{46}O_2)$	366.62	24
Linoleic	$(C_{18}H_{32}O_2)$	280.45	18
Linoelaidic	$(C_{18}H_{30}O_2)$	280.45	18
<u>a-Linolenic</u>	$(C_{18}H_{30}O_2)$	278.43	18
Arachidonic	$(C_{20}H_{32}O_2)$	304.47	20
Eicosapentaenoic	$(C_{20}H_{30}O_2)$	302.451	20
Docosahexaenoic	$(C_{22}H_{32}O_2)$	328.488	22

1	Table 1: T	he chemical	formula and	molecular	weight of	the studied	acids
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Many methods estimating these parameters have been proposed in literature, and the group- contribution approach was generally used for the prediction of physicochemical properties of pure organic compounds, where a compound or a mixture of compounds is considered as a solution of groups and its properties are the sum of the contribution of each group. In this technique, it is assumed that some property is a function of the molecule structure, e.g. the number and types of chosen molecular structures each of which is assigned a numerical value. Examples of such methods include those of Lydersen

[22], Joback and Reid [23], Ambrose [24], Klincewicz-Reid [25] Ma Peisheng et al. [26] and Fedors [27]. Even if these correlations are able to estimate the properties quite rapidly, many of them fail in distinguishing among isomers due to the oversimplification of the molecule structure or, in extrapolating to long chain paraffins. More recently, Constantinou and Gani [28] and Marrero and Gani [29] improved the methods by introducing in their methods new groups allowing the describing of the various molecular structures and their isomers. In the same context, in 2010 Mauricio Sales-Cruz et al. [30] verified the use of available group contribution correlations, to estimate critical temperatures T_C (K), critical pressures P_C (bar) and critical volumes V_C (cm³/mol) of pure hydrocarbons, able to fit the data with relatively small errors. They used three group contribution methods to estimate the critical properties of some fatty acids. The mentioned groups are Joback-Reid (JR), Constantinou-Gani (CG) and Marrero-Gani (MG), which are available in commercial simulators (such as Aspen Plus and ICAS). The studied fatty acids in [30] are caprylic acid, C8:0; capric acid, C10:0; lauric acid, C12:0; myristic acid, C14:0; palmitic acid, C16:0; stearic acid, C18:0; oleic acid, C18:1; linoleic acid, C18:2; linolenic acid, C18:3. So, it is important to compare our results with those of the mentioned work [30] for the mentioned above fatty acids.

It should be mentioned here, that the construction of the methodology requires the selection of suitable algorithms for determining the indicated above properties and to demonstrate the effectiveness of this selection on the example of some acids.

2.1. Latent heat of vaporization

For evaluating the latent heat of vaporization ΔH_v , Pitzer *et al.*, [31,32] showed that ΔH_v can be correlated to Tc, Tr, and ω expressed by the following equation:

 $\Delta H_{\rm v} / (RT_{\rm c}) = 7.08(1 - T_{\rm r})^{0.354} + 10.95 \,\omega \,(1 - T_{\rm r})^{0.456} \tag{1}$

where ΔH_v is in the units of (J/mol); Tc is the critical temperature (K); T_r is the reduced temperature = T/Tc; $\boldsymbol{\omega}$ is the acentric factor $\boldsymbol{\omega} = \alpha/\beta$ where:

 $\alpha = -ln \ Pc{-}5.97214 + 6.09648 \theta^{-1} \ + 1.28862 \ ln \ \theta \ - \ 0.169347 \ \theta^6$

 $\beta = 15.2518 - 15.6875 \ \theta^{-1} - 13.4721 \ \ln \theta + 0.43577 \ \theta^{6}$

 θ being the reduced boiling temperature $T_{br} = T_b/T_c$, Pc is the critical pressure (bar); T_b is the Normal boiling point (K) and R is the gas constant. Reid et al. [17] studied eq. (1) and claimed that it should be used for high temperature predictions where $0.6 < T_r < 1.0$. To predict the latent heat of vaporization at low temperatures, Fish and Lielmezs [33] suggested another formulation as follows:

 $\Delta H_{v} = (\Delta H_{vb}/1000) (T_{r}/T_{br})(X + X^{q})/(1 + X^{p})$ (2) where

 $X = (T_{br}/T_r)(1 - T_r)/(1 - T_{br})$

where parameters q and p are 0.35298 and 0.13856 respectively for organic liquids and ΔH_{vb} is the latent heat of vaporization at the normal boiling point which could be calculated using the Giacalone equation [34]:

$$\Delta H_{vb} = RT_c T_{br} \ln(P_c/1.01325)/(1-T_{br})$$
(4)
or Riedel method [34]:

 $\Delta H_{vb} = 1.093 RT_c T_{br} (\ln(P_c) - 1.013) / (0.930 - T_{br})$ (5) or Chen method [34]:

 $\Delta H_{vb} = RT_c T_{br}(3.978T_{br} - 3.958 + 1.555 \ln P_c)/(1.07 - T_{br}) \quad (6)$ or Vetere method [34]:

 $\Delta H_{vb} = RT_cT_{br}(0.4343 \ln P_c - 0.69431 + 0.89584T_{br})/$

$$0.37691 - 0.37306 T_{br} + 0.15075 P_c^{-1} (T_{br})^{-2}$$
(7)

(3)

To utilize the Fish and Lielmezs method, the latent heat of vaporization at the normal boiling point has to be first calculated using the four prediction methods (Eqs. (4)–(7)). The calculated latent heat of vaporization of all studied acids at the normal boiling point regarding critical properties calculated using Lydersen method [22] are given in Table 2. The latent heat of vaporization for studied acids was predicted and compared over two prediction methods: Pitzer method, and Fish and Lielmezs method. The same input parameters of critical temperature, acentric factor and normal boiling temperature were used. Figure 1 presented these results in the case of palmitic

acid. It can be seen from Fig. 1 that the Pitzer method gives higher values by about 10% regarding different forms of Fish and Lielmezs method. Table 2 gives the predicted results using different methods at temperatures where experimental data are available.

Table 2:	The predicted acentric factor ω as well as the latent heat of
	vaporization ΔH_{vb} (J/mole) using critical properties calculated
	by Lydersen method [22].

Aliphatic acid	Giacalone	Riedel	Chen	Vetere	Pitzer	[17–21]
formic acid	39301	41390	40851	40603.4	45987	2010 0
Acetic acid	39786	41599	40885	40861	47071	23700
Propinionic acid	419016	43607	42666	42813	50805	30984
Butyric	44172	45846	44632	44923	54811	40450
valeric	466592	48373	46826	47239	59219	73200 ± 2000
Caproic	49021	50831	48893	49405	63461	46600±3000
Enanthic	51531	53505	51099	51691	68010	48500
Caprylic	53641	55821	52892	53537	71905	
Pelargonic	56155	58616	55066	55746	76552	52000±3000
Capric	58520	61305	57070	57759	80975	53600±3000
Lauric	62994	66528	60757	61377	89452	56.6±3.0
Myristic	63453	67520	60529	60929	90584	59300
Palmitic	71379	76295	67364	67455	105631	617 00
Stearic	72191	77061	67451	67090	107449	63800±3000
Arachidic	67737	71603	62720	61890	99332	65800±3000
Behenic	78105	80921	71743	701781	118851	67700±3000
Lignoceric	78275	78621	71371	69197	118993	69300±3000
Cerotic	78583	75745	71111	68371	118916	70900±3000
Myristoleic	67048	71444	64081	64575	97193	64000±6000
Palmitoleic	72907	78069	68930	69114	108425	67000±6000
Sapienic	73614	78826	69598	69785	109741	67715
Oleic	72582	77672	67929	67666	108133.7	67395
Vaccenic	76962	82359	72028	71749	116332	71200±6000
Elaidic	72582	77672	67929	67666	108134	
Erucic	72159	75102	66375	65035	107794	69700±6000
Nirvonic	79454	80257	72546	70449	121191	81400±6000
Linoleic	78356	84053	73455	73278	118891	66600±6000
Linoelaidic	73180	78682	68719	68652	109156	66597
α-Linolenic	79135	85084	74310	74238	120299	76900±6000
Arachidonic	78271	83830	72921	72413	118940	72300±6000
Eicosapentaenoic	82245	88350	76744	76328	126343	76300±6000
Docosahexaenoic	81806	86936	75790	74869	125688	77300±6000

It is seen from Table 2 that, with exclusions the predicted results for formic, acetic and propinionic acids, the results of Chen and Vetere equations are comparable with the experimental data. On the other hand, as experimental data, concerning the latent heat of

vaporization ΔH_v at different temperatures, are not available it is difficult to mention which of these two methods, Pitzer et al. [31, 32] or Fish and Lielmezs [33], is more accurate. Although overall the Fish and Lielmezs method is less accurate as mentioned by Reid *et al.*, [17], the prediction accuracy, proved in this work, is fairly good and better than that of Pitzer *et al.*, (see table 2).





2.2. Heat of combustion

In modeling biomass reactions and reactors it is necessary to have values for the heats of formation and combustion of the various materials considered. In some cases, the composition of carbonaceous materials is known or can be estimated, while the heats have not been measured. Concerning different approaches which are used to evaluate the heat of combustion one can mention that formula developed by the Institute of Gas Technology (IGT) in 1978 for predicting heat of combustion of coal [35]:

 $\Delta H_c \text{ (Btu/lb)}=146.58 \text{ C}+568.78 \text{ H}-51.53 \text{ (O+N)}-6.58 \text{ A}+29.45 \text{ S} \quad (8) \\ \text{where C, H, O, N, S, and A are the weight' percents of carbon,} \\ \text{hydrogen, oxygen, nitrogen, sulfur, and ash respectively. This}$

equation was derived by correlating the thermal data with the composition on more than 700 samples of coal.

In the Survey of Biomass Gasification [36], Graboski and Bain used this formula, as well as two others, on 15 samples of biomass and 5 samples of char and found average errors from the measured values of 1.7% and 2.1% respectively. The error of actual measurements of composition and heats of combustion probably exceeds this, so that this suggests that the method can be used for all biomass solids. Later on, the IGT formula was extended to a wide variety of carbonaceous materials. The equation in the modified SI form is:

 $\Delta H_c(kJ/g) = 0.341 \text{ C} + 1.322 \text{ H} - 0.12 (O+N) - 0.0153 \text{ A} + 0.0686 \text{ S} \quad (9)$ where the last two terms are, generally, very small compared to the

first three. The other two equations used by Graboski and Bain [36] are the historical Dulong Berthelot equation:

 $\Delta H_{c}(Btu/lb) = 146.76 \text{ C} + 621 \text{ H} - (N+O-1)/8 + 39.96 \text{ S}$ (10) and that of Tillman [37]:

 $\Delta H_{c}(Btu/lb) = 188 \text{ C-718}$

(11)

According to the first principal of thermodynamics regarding reactions involving in condensed phases and a gaseous phase, the oxygen decreases both the theoretical air required to complete combustion of the fuel and its heating value, since it is chemically combined with hydrogen and carbon atoms [38]. The ΔH_c reduction per kilogram of oxygen would be 17.9 MJ/kg if combined with H, or 12.3 MJ/kg if combined with C. So, it is now understood why the empirical value of 15 MJ/kg is often used. This gives for the mass-percentages composition the following formula:

 $\Delta H_{c} (MJ/kg) = 0.33 \cdot \% C + 1.43 \cdot \% H - 0.15 \cdot \% O$ (12)

When applying these formulae to different aliphatic acids and comparing the calculated results with available experimental data [39] it was found that:

- The historical Dulong Berthelot equation (eq. (10)) overestimates the heat of combustion (see Table (3)).
- The Tillman equation (eq. (11)) underestimates the heat of combustion and no need to include its results in Table (3).
- The IGT formula as well as its modified form gives nearly the same results (see table (3)).
- Regarding available experimental data that proposed in this work a formula for predicting the heat of combustion of aliphatic acids gives less relative error compared with experimental results.

• The IGT formula, its modified form and that proposed in this work are applicable for predicting the heat of combustion of aliphatic acids. one obtains values given in Table 3.

Thus, it seems from Table (3) that equation (12), among the above equations, gives a relative error less than 5% in studied acids (except formic acid) and less than 2% in the main components of soybean oil. So, it forms a reliable basis for predicting biomass thermo-chemical data where measured heats are not available, and can form a supplement to the representative heats of combustion shown in this publication.

Tuble et impud		0			
Aliphatic acid	[39]	eq(8)	eq(9)	eq(10)	This work
formic acid	60.90	69.37	69.23	166.76	48.29
Acetic acid	209.19	230.46	230.29	333.80	211.36
Propinionic acid	365.42	391.64	391.44	500.93	374.51
Butyric	522.52	552.86	552.63	668.10	537.70
valeric	678.98	714.03	713.76	835.20	700.84
Caproic	835.64	875.27	874.97	1002.39	864.07
Enanthic	992.18	1036.45	1036.12	1169.50	1027.22
Caprylic	1148.67	1197.71	1197.35	1336.70	1190.46
Pelargonic	1305.52	1358.89	1358.50	1503.81	1353.62
Capric	1462.31	1520.15	1519.73	1671.02	1516.86
Lauric	1774.82	1842.68	1842.20	2005.42	1843.34
Myristic	2087.99	2165.17	2164.62	2339.78	2169.79
Palmitic	2401.43	2487.62	2487.02	2674.11	2496.21
Stearic	2714.68	2810.19	2809.52	3008.55	2822.73
Arachidic	3027.83	3132.66	3131.92	3342.88	3149.15
Behenic	3342.69	3455.13	3454.33	3677.22	3475.58
Lignoceric		3777.59	3776.74	4011.56	3802.01
Cerotic		4100.17	4099.25	4346.01	4128.54
Myristoleic		2101.79	2101.29	2270.58	2101.29
Palmitoleic		2424.23	2423.67	2604.89	2427.69
Sapienic		2424.25	2423.69	2604.91	2427.71
Oleic		2746.71	2746.09	2939.25	2754.13
Vaccenic		2746.72	2746.10	2939.26	2754.14
Elaidic		2746.71	2746.09	2939.25	2754.13
Erucic		3391.74	3390.99	3608.02	3407.07
Nirvonic		3714.21	3713.40	3942.36	3733.50
Linoleic		2683.33	2682.76	2870.05	2685.63
Linoelaidic		2702.64	2702.06	2890.70	2704.95
α-Linolenic		2619.86	2619.33	2800.76	2617.04
Arachidonic		2878.95	2878.40	3065.90	2874.96
Eicosapentaenoic		2815.49	2815.00	2996.62	2806.38
Docosahexaenoic		3074.55	3074.04	3261.73	3064.28

Table 3: Alipatic acids heat of combustions Δ Hc (Kcal/mol).

Note: Contrary to the most available in literature works, [39] gives negative signal for the energy of combustion. This means that he supposed that negative energy values are related to liberated heats from the system while positive energy values are related to provided heats to the system.

2.3. Liquid heat capacity

Noor Azian Morad et al. [40] mentioned that the liquid specific heat capacity of fatty acids can be accurately estimated using the Rowlinson-Bondi method [17] which requires specific heat capacity of ideal gases, critical temperature, and acentric factor for each acid. It is claimed in [40] that the estimated values were compared to experimental values and the error was found to be within $\pm 5\%$.

The Rowlinson-Bondi equation was used to estimate specific heat capacity (C_p) for pure component fatty acids. The equation, as quoted in Reid et al., [17], is as follows:

 $(C_p - C_{po})/R = 1.45 + 0.45 (1 - T_r)^{-1}$

 $+0.25 \ \omega [17.11+25.2 \ (1-T_r)^{1/3} T_r^{-1} + 1.742 \ (1 - T_r)^{-1}]$ (13) where C_p is the liquid specific heat capacity, C_{po} is the ideal gas specific heat capacity, R is the universal gas constant, T_r is the reduced temperature, and ω is the acentric factor. The dependence of the left part of eq. (13) on temperature, on the example of palmitic and stearic acids is shown on Fig. 2. The unknown value in (13) is C_{po} which should be determined.



Figure 2: The dependence of the heat capacity C_p of palmitic acid (\blacklozenge) and stearic acid (
) on Temperature using Rowlinson-Bondi equation.

Here it should be mentioned that the Joback method uses four parameter polynomial to describe the temperature dependency of the ideal gas heat capacity (C_{p0}):

$$C_{p0} = (\sum n_j \Delta_a - 37.93) + (\sum n_j \Delta_b + 0.210)T + (\sum n_j \Delta_c - 3.91x10^{-4})T^2 + (\sum n_j \Delta_c + 2.06x10^{-7})T^3$$
(14)

where n_j is the number of groups of the jth type and Δ_c are contributions for the jth atomic or molecular group. The temperature T is in Kelvin and the heat capacity is in (J/mol.K). These polynomial parameters are valid from 273 K to approximately 1000 K. Choosing the same atomic and molecular groups Joback et al. [23] proposed values given in Table 4 to obtain group contributions to estimate polynomial coefficients. When applying the mentioned method for calculating the dependence of heat capacity on temperature, on the example of palmitic and stearic acids, it was found the results presented in Figure 3.



Figure 3: The dependence of the ideal gas heat capacity C_p of palmitic acid (-) and stearic acid (+) on temperature using Joback method.

Method		-СНЗ	-СН2-	=CH-	-COOH
	Δ_{a}	19.5	2.36E+1	-8.00	2.41E+1
Johools mothod	$\Delta_{\rm b}$	-8.08E-3	3.81E-2	1.05E-1	4.27E-2
JODACK IIICHIOU	$\Delta_{\rm c}$	1.53E-4	1.72E-4	-9.63E-5	8.04E-5
	$\Delta_{\rm d}$	-9.67E-8	-1.03E-7	3.56E-8	-6.87E-8
	A _{1k}	-1.1369	-0.0691	0.0472	-0.6459
	A _{2k}	-0.00003	0.00003	-0.00021	-0.0104
	B_{1k}	83.6969	54.7992	12.9121	108.8
	B_{2k}	0.0109	-0.0101	0.0518	13.1121
Ceriani method	C _{1k}	-72.3043	2.7245	3.272	-102.2
	C _{2k}	-3.439	4.2745	8.2213	828.0
	f ₀	f_1	α	β	γ
	-3.5733	0.2758	0.00127	0.6458	-273.5

Table 4: The group contributions of various atoms or groups of atoms

2.4. Liquid density

There are a number of methods for predicting the liquid density of compounds and their mixtures. The most important and accurate among them is the modified Rackett method [17]. According to this technique:

 $V_{s} = (RT_{c}/P_{c})(Z_{RA})^{\phi}$ (15) Where $\phi = [1 + (1 - Tr)^{3/7}], V_{s}$ is the molar volume of the saturated critical solutions, R is the gas ideal constant, T_c is the estimated critical temperature, P_c is the estimated critical pressure and T_r is the reduced temperature. Z_{RA} is the Rackett parameter, a correlating parameter unique to each compound and is determined experimentally. Values of Z_{RA} are given in Table 5 where the letter in the brackets stands for the used method: A for Ambrose, J for Joback, L for Lyderson, M for Ma Peisheng and K for Ma Peisheng. When comparing Z_{RA} calculated values using Ma Peisheng et al. [26] and Lydersen [22] methods with those presented in [30] it is found that a good agreement between them (see Table 5). The pure compound (saturated) liquid density (ρ) is evaluated as follows:

$$\rho = M/V_s$$

(16)

where M is the molecular weight.

It is worth mentioning that the original Rackett equation employs the compressibility factor Z_c instead of Z_{RA} as proposed by Spencer and Danner [30]. However this last method has been demonstrated to be more accurate [30]. Nonetheless, values of Z_c and Z_{RA} are similar. Secondly, the densities were predicted according the modified Rackett equation. Values of Z_{RA} for some FA were reported in [30], where it is mentioned that Z_{RA} values were calculated by solving the modified Rackett equation (15) directly for Z_{RA} with a reference density at a

given temperature. However, when eqs (15) and (16) are used for calculating the density of palmitic and stearic acids, it was found that these method underestimates the density regarding to available experimental data.

Aliphatic acid	7 (A)	7 (I)	7 (I)	7 (M)	7 (K)	[30]
Aliphatic actu	$L_{RA}(A)$	$L_{RA}(J)$	$L_{RA}(L)$	$\mathcal{L}_{RA}(\mathbf{NI})$	$L_{RA}(\mathbf{K})$	
formic acid	0.259501	0.248418	0.24/859	0.259804	0.246/61	
Acetic acid	0.256414	0.245663	0.24589	0.260862	0.247397	
Propinionic acid	0.252931	0.239828	0.242838	0.259165	0.244627	
Butyric	0.249231	0.233858	0.239061	0.257422	0.24172	
valeric	0.245416	0.227792	0.23477	0.255656	0.238919	
Caproic	0.241549	0.221678	0.230114	0.253723	0.236526	
Enanthic	0.23767	0.215571	0.225208	0.251732	0.234504	
Caprylic	0.233807	0.209533	0.220158	0.249298	0.233237	0.24920
Pelargonic	0.229979	0.203631	0.215064	0.246989	0.232673	
Capric	0.226199	0.197943	0.210025	0.244397	0.232967	0.24426
Lauric	0.218817	0.187538	0.200535	0.238479	0.236259	0.23983
Myristic	0.211708	0.179029	0.192551	0.225373	0.243451	0.23466
Palmitic	0.204891	0.173148	0.186943	0.225214	0.25269	0.22953
Stearic	0.198374	0.170558	0.184495	0.212229	0.264552	0.22467
Arachidic	0.192156	0.17174	0.185767	0.178832	0.277592	
Behenic	0.186231	0.176882	0.19097	0.202618	0.289312	
Lignoceric	0.180591	0.185814	0.199897	0.195845	0.300757	
Cerotic	0.175226	0.198008	0.211945	0.194742	0.310628	
Myristoleic	0.207608	0.184102	0.192546	0.23003	0.241928	
Palmitoleic	0.200882	0.177348	0.186691	0.226382	0.249905	
Sapienic	0.200882	0.177348	0.186691	0.227556	0.249838	
Oleic	0.194392	0.173653	0.18393	0.211557	0.260835	0.21939
Vaccenic	0.194392	0.173653	0.18393	0.221018	0.260461	
Elaidic	0.194392	0.173653	0.18393	0.211557	0.260835	
Erucic	0.182195	0.177368	0.189709	0.17852	0.285365	
Nirvonic	0.176496	0.185016	0.198334	0.197061	0.296617	
Linoleic	0.190378	0.177076	0.183394	0.221967	0.257021	0.22550
Linoelaidic	0.186238	0.1808	0.182887	0.209657	0.254607	
α-Linolenic	0.186238	0.1808	0.182887	0.221675	0.254075	0.22840
Arachidonic	0.175924	0.181278	0.182293	0.206074	0.303325	
Eicosapentaenoic	0.171402	0.184521	0.181502	0.212922	0.308534	
Docosahexaenoic	0.161139	0.185768	0.183835	0.199544	0.315816	

Table 5: The predicted Rackett parameter for some fatty acids FA.

Reid *et al.*, [17] gave another version of Rackett equation for estimating the molar volume of saturated liquids:

$$\mathbf{V}_{\mathrm{S}} = \mathbf{V}_{\mathrm{S-R}}(\mathbf{Z}_{\mathrm{RA}})^{\Phi} \tag{17}$$

where

$$\phi = (1 - T_r)^{2/7} - (1 - T_{r-R})^{2/7}$$
(18)

 V_{S-R} being the experimental V_S at reference temperature T_R ; T_{r-R} is the reduced temperature at reference temperature T_R ; and V_{S-R} is a unique constant for each compound. The above formula can be transformed into:

 $\rho = \rho_R/(Z_{RA})^{\phi}$ (19) where ρ_R is the experimental density value (g/cm³) at reference temperature T_R . To find out the value of Z_{RA} , another experimental density value at a different temperature should be required besides the experimental density value at the reference temperature T_R . The estimated liquid densities for palmitic and stearic acids are given on Fig 4.

Daubert *et al.*, [41] proposed data compilation method for estimating the liquid density:

 $\rho = A/B^{s1} \tag{20}$

where $s_1 = 1 + (1-T/C)^D$, ρ being the liquid density (g/cm³), and the constant values of A, B, C and D can be found in the Data Compilation [41].



Figure 4: Temperature liquid density dependence of myristic (♦), palmitic (■), stearic (x), oleic (▲) and linoleic (𝔅) acids using Reid et al. method.

2.5. Liquid viscosity

Orrick and Erbar proposed a method [17] which employs a group contribution method and it is assumed to be suitable to estimate the liquid viscosity at low temperatures ($T_r < 0.75$). It assumes a linear relationship between the logarithm of viscosity and the reciprocal of temperature.

 $Ln(\eta/M \rho) = A + B/T$ (21)

where η is the liquid viscosity (mPa*s); ρ is the liquid density at 20 °C (g/cm³); the constant values of A and B should be calculated using the group contribution method in [17]. Above the reduced temperature of about 0.7, Letsou and Stiel method [17] mentioned that the assumption that Ln(η) is a linear function of the reciprocal absolute temperature is no longer valid. Hence they proposed the following procedure for liquid viscosity prediction:

$\eta = [(\eta)^{(0)} + \omega (\eta)^{(1)}]/\zeta$	(22)
$(\eta)^{(0)} = 10^{-3} [2.648 - 3.725 T_r + 1.309 (T_r)^2]$	(23)
$(\eta)^{(1)} = 10^{-3} [7.425 - 13.39T_r + 5.933(T_r)^2]$	(24)
$\zeta = 0.176 (T_c/M^3)^{1/6} / (P_c)^{2/3}$	(25)

where η is the liquid viscosity (mPa*s). According to Data Compilation method [41] the liquid viscosity can also be found in: $\ln \eta = A + B/T + C \ln T$ (26)

where η is the liquid viscosity (mPa* s), and the constant values of A, B and C can be found in [41].

Roberta Ceriani et al [42] proposed a method suitable for prediction the viscosities of fatty compounds and biodiesel by group contribution. According to this method:

 $\ln\eta(mPa^*s) = \sum N_k (A_{1k} + B_{1k}/(T(K) + C_{1k}))$

+
$$M \sum N_k (A_{2k} + B_{2k} / (T(K) + C_{2k}) + Q$$
 (27)

where N_k is the number of group k in the molecule, M is the molecular weight, A_{1k} , A_{2k} , B_{1k} , B_{2k} , C_{1k} , C_{2k} are parameters given in Table 4 and Q is a correction term having, in the case of aliphatic acids, the form:

$$Q = (f_0 + N_c f_1)[\alpha + \beta/(T(K) + \gamma)]$$

(28)

 N_c is the number of carbon atoms in the molecule and f_0 , f_1 , α , β , γ are parameters given in Table 4.





To evaluate the liquid viscosity prediction models introduced previously, the predicted liquid viscosity was compared with the experimental liquid viscosity values reported in literature. Here it was found that, a significant deviation in the liquid viscosity prediction has been found within the lower temperature range when the Letsou and Stiel method is applied, whereas, the results obtained by Orrik and Erbar method is very close to the liquid viscosity reported in Data Compilation over the entire temperature domain. Hence, it is believed that the Orrick and Erbar method is more suitable than that of Letsou and Stiel for the liquid viscosity estimation over a large temperature range. On the other hand, when applying the method of Ceriani et al a better agreement with available experimental data is achieved. The calculated results, using this method, are presented in Fig 5. In order to compare with experimental data for different temperature values one can find some values related to propinionic acid. Table 6 gives the available experimental values with corresponded predicted values.

Table 6: Predicted and measured liquid viscosity (mPa*s) of propinionic acid.

	15°C	25°C	30°C	60°C	90°C
Experimental value	1.175	1.020	0.956	0.668	0.495
Predicted value	0.956	0.923	0.906	0.819	0.748

2.6. Liquid thermal conductivity

Latini *et al.*, proposed a method [17] for predicting the thermal conductivity of organic materials:

 $\lambda = A(1 - T_r)^{0.38} / (T_r)^{1/6}$ $A = A^* (T_b)^{\alpha} / M^{\beta} / (T_c)^{\gamma}$

where λ is the liquid thermal conductivity (W/m K); parameters A^{*}, α , β , and γ can be found in [17]. On other hand, Sato [17] suggested that, at the normal boiling point, (31)

 $\lambda (T_{\rm b}) = 1.11/{\rm M}^{0.5}$

where λ (T_b) is the thermal conductivity of the liquid at the normal boiling point (W/m K). To estimate λ at other temperatures, the Riedel equation shown below can be used:

$$\lambda = B[3 + 20(1 - T_r)^{2/3}]$$

(32)

(29)

(30)

Combing the above equations, we have:

 $\lambda = (1.11/M^{0.5})[3 + 20(1 - T_r)^{2/3}]/[3 + 20(1 - T_{br})^{2/3}]$ (33) The liquid thermal conductivity (W/m K) can be estimated using

data compilation method [41]:

 $\lambda = A + BT$ (34)

where the constant values of A and B can be found in [41]. Fig. 6 gives the predicted liquid thermal conductivity of myristic acid, palmitic acid, stearic acid and oleic acid.

2.7. Surface tension

For predicting the surface tension one can use Macleod-Sugden correlation [17]:

 $\sigma = ([P]\rho_b)4 [(1 - T_r)/(1 - T_{br})]^{4n}$ (35)

where σ is the surface tension (dyn/cm); [P] can be calculated from [17]; ρ_b is the molar liquid density at the normal boiling point (mol/cm^3) ; and 4n = 1.24 for all organic compounds [17].



Figure 6: The dependence of the liquid thermal conductivity of myristic acid (♦), palmitic acid, (■) stearic acid (▲) and oleic acid (𝔅) on temperature using Riedel equation.

Another attractive method called corresponding states correlation [17] can be used for the same purpose:

 $\sigma/[(P_c)^{2/3}(T_c)^{1/3}] = (0.132\alpha_c - 0.279)(1 - T_r)^{11/9}$ (36) where $\Box c$ is the Riedel parameter:

 $\alpha_{\rm c} = 0.9076 \left[1 + T_{\rm br} \ln(P_{\rm c}/1.01325)/(1 - T_{\rm br}) \right]$ (37)

Moreover, data compilation can be used for predicting the surface tension values [41] as follows:

$$\sigma = A(1 - Tr)^{s'}$$
(38)
s' = B+CT_{br} + D(T_{br})²+E(T_{br})³ (39)

where σ is the surface tension (N/m), and the constant values of A, B, C, D and E can be found in Data Compilation [41].

The predicted surface tension of palmitic and stearic acids using corresponding states correlation [17] are shown in Fig. 7. It is found that the Corresponding States correlation is more accurate for the prediction compared to the Macleod–Sugden correlation. The percentage deviation resulted from the Corresponding States correlation increases with the decreasing temperature, and the largest percentage deviation is about 3% at the temperature of 300 K.



Figure 7: The dependence of the liquid surface tension of palmitic acid (▲) and stearic acid (x) on Temperature using corresponding states correlation [17].

3. Conclusions

In this work, a detailed physical properties prediction has been done for aliphatic acids. For each physical property, the best prediction model has been identified and the calculated properties can be used as key references for biodiesel combustion modeling. The following conclusions have been made based on the results obtained above:

- (1) For latent heat of vaporization prediction, the Pitzer method has been found to be more suitable than the Fish and Lielmezs method. So, it should be used in modeling.
- (2) For the heat of combustion prediction, the proposed equation (12) forms a reliable basis for predicting biomass thermo-chemical data where measured heats are not available, and can form a supplement to the representative heats of combustion shown in this publication. So, equation (12) should be used in modeling.
- (3) The Rowlinson-Bondi equation was used to estimate specific heat capacity (C_p) for pure fatty acids and it could used be in modeling in first approximation.

- (4) It is found that the Rackett method has a good predictability on liquid density and it will be used in modeling. The key to a successful prediction lies on a careful selection of the two reference densities required by the Rackett method.
- (5) Three prediction models have been compared and evaluated for the liquid viscosity prediction. It is found that the Roberta Ceriani method is more suitable for the liquid viscosity estimation over a large temperature range. So, it should be used in modeling.
- (6) For liquid thermal conductivity, the predicted results using the Riedel equation in combination with Sato proposal match well with measured values of soybean oils. So, it should be used in modeling. Based on this method, the liquid thermal conductivity has been calculated for the four acids.
- (7) The Corresponding States correlation is more accurate for the surface tension prediction than the Macleod-Sugden correlation. The largest percentage deviation resulted from the Corresponding States correlation is about 3% at the lowest expected temperature of the fluid. This result matches well with that of [43]. Therefore, this correlation should be used in modeling.
- (8) After constructing this methodology and calculating the critical and physical properties of the main aliphatic acids the prediction of the critical and physical properties of known vegetable oils and animal fats is possible. This will be a subject of other publication.

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