

The prediction of critical parameters for triolein, diolein, monoolein and methyl esters

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ABSTRACT

Prediction and preliminary modelling of equilibrium data represents the best tool for obtaining the real picture of reaction system when the experimental data are not available or can not be easily measured. The complex reaction mixture under supercritical condition is one such system and for its modelling two main problems usually exists. The first is the approximation of real data at critical point, and the second is the asymmetry of the mixtures due to large differences in both size and attractive forces between the supercritical solvent and solute molecules. Triolein, one of the typical triglycerides, is the most abundant component in many plant oils, such as sunflower, canola, soybean, rapeseed, which are mostly used as feed in synthesis of fatty methyl esters (FAME or biodiesel). Nowadays the biodiesel synthesis starts to be very important in the case of vegetable oil (triolein) alcoholysis under supercritical condition of methanol. The reaction is performed in three steps including several intermediary products /reactants (diolein, monoolein) which are reactants for obtaining the methyl oleate and glycerol as the final products.

In this study the critical parameters, as well as acentric factor of triolein, diolein, monoolein and methyl oleate were estimated by using Aspen software. The group contribution method suggested by Constantinou and Gani [1, 2] had been used to predict the critical parameters. The method is based on molecular structure and represents addition of group contribution influence in the molecule (the first order and second order group). This method is very useful for prediction the normal boiling point of pure compound which are one of the most important parameter for estimation other critical parameters. However, the normal boiling point of triolein cannot be determined experimentally due to its thermal decomposition at temperatures even below its boiling point. Some thermodynamical data of analyzed components are given in the literature, and exists in well prepared data base, e.g. in Aspen or DIPRR data base. Estimations of critical parameters realized in this study were compared to available data in Aspen and DIPRR base. The importance of valid value of critical parameters and their use in the process of Aspen simulation of biodiesel production under supercritical condition was pointed out in this study.

INTRODUCTION

In process simulation, reliable and accurate property estimation methods play an important role in the solution of various simulation problems where convergence is often traced to failures in the reliable predictions of physical and thermodynamic properties. In the literature there are a several papers with this subject [1-11] and they proposed, for the estimation of physical and thermodynamic properties of pure compounds, the group contribution methods as the most accurate one. According to these methods, the property of a compound could be estimated as a summation of the contributions of first- and second-order groups which are defined by specific molecular structure. They provide the important

advantage of quick estimates without requiring substantial computational resources. This method is very important for calculating the normal boiling point (for many organic compounds are not available in literature) which is essential in separation processes and for the estimation of the critical temperature. Also, the molecular structure is often oversimplified, making isomers indistinguishable.

In this paper the group contribution method was used [1, 2] which is based on estimation the influence of the first- and second-order groups of complex molecule structure. The structure of a functional second-order group should have adjacent first-order groups as building blocks. The performance of second-order groups is independent of the molecule in which the groups occur, satisfying a fundamental group-contribution principle. The method was applied to the following physical and thermodynamic properties of pure compounds estimation: the normal boiling point, the normal melting point, the critical pressure, the critical temperature, the critical volume, the standard enthalpy of vaporization at 298 K, the standard Gibbs energy, the standard enthalpy of formation at 298 K, the acentric factor and liquid molar volume at 298 K. Estimations of critical parameters realized in this study was compared to corresponding available data proposed by Aspen and DIPRR base.

MATERIAL AND METHODS

Triolein, one of the typical triglyceride, is the most abundant component in many plant oils, such as canola, soybean, sunflower seed, etc. In this study, the physical and thermodynamic properties of pure triolein as well as of diolein, monoolein and methyl oleate were estimated. The parameters of these compounds which are main representative of biodiesel could be found in Aspen and DIPRR data bases.

The base equation for estimating the thermodynamic and physical parameters for triolein, diolein, monoolein, and methyl esters can be described as a simple function of the property X :

$$f(X) = \sum_i N_i C_i + \sum_j M_j D_j$$

where C_i is the contribution of the first-order group type- i which occurs N_i times and D_j is the contribution of the second-order group type- j with M_j occurrences in a compound. The left side of above equation, i.e. the $f(X)$ function, used for calculating the specific properties are summarized in **Table 1**.

Table 1. Function $f(X)$ for each analyzed parameter

Parameter	Left side of equation, $f(X)$
T_C , K	$\exp(T_C/181.128)$
P_C , bar	$(P_C - 1.3705)^{-0.5} - 0.10022^{-0.5}$
V_C , m ³ /kmol	$V_C + 0.00435$
T_m , K	$\exp(T_m/102.425)$
T_b , K	$\exp(T_b/204.359)$
ΔG_f (298K), kJ/mol	$\Delta G_f + 14.828$
ΔH_f (298K), kJ/mol	$\Delta H_f - 10.835$
ΔH_v (298K), kJ/mol	$\Delta H_v - 6.829$
ω^1	$\exp(\omega/0.4085)^{0.505} - 1.1507$
V_l (298K), m ³ /kmol	$V_l - 0.01211 \text{ m}^3/\text{kmol}$

RESULTS

The knowledge of phase equilibria under the various conditions of operation at high pressure, covering a wide range of temperatures is obviously important and necessary information for process development, design and optimization. Among many factors that can affect the prediction of vapor–liquid equilibria of organic compounds in supercritical methanol using EOS, evidently, the lack of experimental data of critical properties and acentric factor is most important.

The transesterification of vegetable oils, the esterification of fatty acids and alcoholysis of glycerides under supercritical condition of light alcohols (methanol and ethanol), are of interest in the production of fine chemicals and biodiesel. The partial miscibility between the reactants and products of these processes have raised interest in the multiple phase behavior under reaction and separation conditions of mixtures of triglycerides and derivatives, fatty esters, alcohols and glycerol.

In the literature there are only few papers [13-15] that proposed and calculated the critical parameters for triolein (**Table 2**). Difference between these data obviously exists as a consequence of different methods used for they calculation. In these papers, the critical parameters for diolein, monoolein and methyl oleate were not used for calculating the phase equilibrium at supercritical conditions.

Table 2. Predicted physical properties of triolein published in literature

References	T _b , K	T _c , K	P _c , bar	ω	V _L , m ³ /kmol
Tang et all, 2006 [13]	879.9 ^a	954.1 ^a	3.602 ^a	1.6862 ^b	0.9717 ^c
Weber at all, 1999 [14]	-	947.1 ^d	4.682 ^d	1.6862	-
Vázquez et all, 2009 [15]	-	1043.3 ^e	4.570 ^e	-	-

^a Estimated by the method of Dohrn and Brunner [16,17]; ^b Acentric factor estimated according to Han and Peng [19]; ^c Calculated by the method Formo et al, 1979 [18]; ^d Calculated by method of Ambrose [3] and Raid [20]; ^e Calculated by method Espinosa [21]

Using the group contribution method (first- and second-order groups) and ASPENplus software some physical and thermodynamic parameters for triolein, diolein, monoolein and methyl oleate were calculated and shown in **Table 3**.

Some physical and thermodynamic parameters which are present in ASPEN and DIPPR data bases are presented in **Table 4**.

As can be seen from data given in **Tables 3** and **4**, there are a large difference between the value of some physical as well as thermodynamic parameters. The most important and significant difference is in the case of calculated acentric factor and normal boiling temperature.

Table 3. The physical and thermodynamic parameters calculated in this study

Parameter	Triolein	Diolein	Monoolein	Methyl oleate
M , g/mol	885.45	621.00	356.55	296.49
T_B , K	827.40	765.03	674.82	595.93
V_B , m ³ /kmol	2.708	1.106	0.533	0.489
V_I (298K), m ³ /kmol	0.958	0.623	0.360	0.341
T_C , K	977.88	920.20	835.06	721.02
P_C , bar	3.34	5.05	10.56	11.03
V_C , m ³ /kmol	3.250	2.830	1.254	1.108
ω	1.9782	1.7632	1.5324	1.0494
ΔG_f (298K), kJ/kmol	-1.8E+05	-3.00E+05	-3.23E+05	-1.20E+05
ΔH_f (298K), kJ/kmol	1.97E+05	8.08E+05	5.69E+05	-6.40E+05
ΔH_v (298K), kJ/kmol	3.02E+05	2.19E+05	9.01E+04	6.36E+04

Table 4. The physical and thermodynamic parameters (Aspen and DIPRR data)

Parameter	Triolein	Diolein	Monoolein	Methyl oleate
M , g/mol	885.45	621.00	356.55	296.49
T_B , K	834.65 1120 ¹	920.00	714.00	617.00
V_B , m ³ /kmol	2.708	1.106	0.533	0.489
V_I (298K), m ³ /kmol	0.974	0.677	0.378	0.341
T_C , K	998 1640 ¹	900 1025 ¹	885	764
P_C , bar	3.34 4.70 ¹	7.92	12.40	12.80
V_C , m ³ /kmol	3.25 3.09 ¹	2.252 2.150 ¹	1.254 1.210 ¹	1.060
ω	1.9782 unknown ¹	2.5810	0.9918	1.0494
ΔG_f (298K), kJ/kmol	-1.72E+05 1.72E+07 ¹	-3.47E+05	-3.02E+05	-1.17E+06
ΔH_f (298K), kJ/kmol	-1.84E+06	-1.42E+06	-9.08E+05	-6.26E+05
ΔH_v (298K), kJ/kmol	-	1.07E+05	6.83E+04	6.36E+04

¹ values different in DIPRR data base from the values in ASPEN

Also the critical temperature and critical pressure calculated by group contribution method are different from corresponding value given in ASPEN and especially in DIPPR data bases. The values of normal boiling points of analysed glycerides and esters are very important data for the adequate and real separation process (especially for distillation process) which represent one step in biodiesel process synthesis and purification (purification of final products and recovery of excess methanol) [22].

Simulation of supercritical biodiesel synthesis (complete process followed by purification of products) which can be realized using ASPEN software and corresponding values of physical and thermodynamic parameters given in ASPEN base will not give reliable results. Namely, the methanolysis of triglycerides occurs in heterogeneous system which exists in more than two phases. The corrected data calculated in this study, together with RK-Aspen equation of state, were used for prediction the phase equilibria between triolein and methanol at elevated pressure and temperature. The simulation of phase equilibria data predicted very well the experimental one [23].

CONCLUSION

In this study the physical and thermodynamic parameters of triolein, diolein, monoolein and methyl oleate were estimated by using Aspen software. The group contribution method based on influence the first- and second order groups present in molecule [1, 2] were used to predict these parameters. Used method is very useful for prediction the normal boiling point of pure compound which are one of the most important parameter for estimation other critical parameters. However, the normal boiling point of triolein cannot be determined experimentally due to its thermal decomposition at temperatures even below its boiling point. Estimations of critical parameters realized in this study were compared to available data in Aspen and DIPPR base. The large difference between calculated value of critical parameters and acentric factor and those presented in both data base obviously exist. The use of correct values of critical parameters is very important in the simulation of biodiesel production under supercritical condition which can be realized using some software like Aspen.

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