APPROACHES TO THERMODYNAMIC PROPERTY CALCULATION OF COMPLEX FLUIDS: LITERATURE REVIEW

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Abstract - Thermophysical properties of industrially complex fluids whose composition is always ill-defined are in practice predicted by using thermodynamic models. To ensure the prediction accurately and reliably, a three-step procedure to obtain the properties of these fluids must be validated. The focus of this study is laid on a short review of tools which can be served for each of the three steps. It should be noted that the tools presented in this work are centered on the ones applicable for highly associating and/or polar fluids. It is also recommended in this work an approach for characterizing a pseudocomponent representative of a complex mixture, e.g. petroleum fluids, biomass fluids, considering the available analytical data. This fully described pseudocomponent can be easily used within any thermodynamic models.

Key words - Thermodynamic models; equations of state; parameterization; fluid characterization; pseudocomponent.

1. Introduction

Accurate and reliable knowledge of phase equilibrium behavior as well as transport properties plays a crucial role in designing and optimizing chemical and biochemical processes [1]. However, properties for a given process are not always obtained by means of experiments, especially when considering a wide range of working conditions for fluids involved into the process. Therefore, the lack of properties is often compensated by having recourse to mathematical models or equations of state (EoS). To use the selected equation of state for estimating thermodynamic properties, it is necessary for an engineer to parameterize the equation. The purpose of this is to calculate characteristic parameters which will be used as inputs for the equation. Yet, the calculation of properties for practically industrial applications is not easily accessible, even having at hand an EoS and a suitable parameterization approach. This is due to the fact that industrial fluids are usually complex fluids that are composed of a large number of ill-defined components. Petroleum-based fluids are typical examples of complex fluids. These fluids typically contain a large range of different hydrocarbons and non-hydrocarbons whose actual composition is only partially identified [2]. Biomass-originated fluids stemming are even more complex than petroleum-originated ones because they contain large amounts of oxygen-containing species, such as ketones, acids, ethers, esters, aldehydes, *etc* [3]. Therefore, to be able to determine the characteristic parameters, an accurate description of complex fluids is needed. This procedure is called fluid characterization. Figure 1 summarizes a procedure for calculating thermophysical properties of a complex fluid of interest.

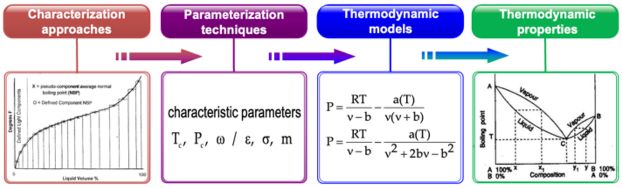

Figure 1. *General procedure for calculating thermophysical properties of a fluid of interest*

As shown in Figure 1, it is crucial to validate three steps in order to be able to calculate phase equilibrium and thermodynamic properties for any mixture:

(i) It requires an adequate EoS or a thermodynamic model for calculating phase equilibrium properties or transport properties.

(ii) The EoS parameters for each component, which constitutes the fluid under consideration, must be at hand. The determination of these parameters should be founded on the chemical nature of the considered component or be relied on experimental means.

(iii) To be able to characterize the considered components, a set of experimental information or analytical information must exist. This information will be used to generate so-called pseudocomponents representing a group of chemical species or representative molecules [4], as commonly applied in petroleum industry. The aim of using this technique, often referred to as "pseudoization", is to reduce the number of actual components present in the fluid of interest. This reduction helps to simplify the calculation and computational cost with the chosen EoS.

This work will perform a short literature review on each of the above-mentioned steps. In the second section, several typical models for thermophysical properties will be presented and discussed. It should be noted that the discussion is focused on predictive equations whose parameters can be purely estimated and on the ones that can be applied for associating and/or polar molecule - containing fluids. The third section will present several parameterization methods which can be used to determine characteristic inputs. In the next section, we will discuss various methods used to define pseudocomponents given the availability of the experimental information. A conclusion is provided in the final section.

2. Equations of state for property calculation

The equations of state can generally be categorized into cubic, statistical mechanics-based, and hybrid EoS.

Being first introduced in 1873 by van der Waals [5], cubic-type equations have since been further modified and are being widely applied in the oil refining industry. The detailed description of the cubic EoS as well as their successful implementation are referred to the works given by Wei and Sadus [6], Valderrama *et al.* [7]. In general, the cubic EoS can be described as the sum of two terms, namely, the repulsive term accounting for the repulsive interactions between hard sphere-type molecules and the attractive term accounting for the attractive interactions between these hard-sphere molecules. Among the most advanced EoS in this category, it is worth mentioning Soave-Redlich-Kwong (SRK) [8] and Peng-Robinson (PR) [9]. These two cubics are widely applied in the petroleum refining industry. Equation (1) is the general expression of the cubic-type equations:

$$P = \frac{RT}{v-b} - \frac{a(T)}{(v-r_1 b)(v-r_2 b)} \tag{1}$$

where r_1, r_2 can take different values depending upon the equation, as shown in Table 1; two characteristic parameters a and b are determined from the critical properties of fluids considered.

***Table 1.** Parameters r_1 and r_2 to be used for cubics including vdW EoS, SRK EoS, and PR EoS*

Parameters	vdW	SRK	PR
r_1	0	0	$-1-\sqrt{2}$
r_2	0	-1	$-1+\sqrt{2}$

The widespread utilization of the cubic EoS is accounted by (*1*) it is simple for these equations to be incorporated into commercial simulation softwares and (*2*) only a few characteristic parameters (*e.g.,* a and b are estimated easily from critical properties) are required for these equations. However, its limitation appears when being used to describe strongly non-ideal mixtures which contain highly polar and/or strongly associating molecules.

Statistical mechanics-based EoS, which allows to linking of bulk properties with molecular properties, is demonstrated to be capable of handling complex mixtures of associating and/or polar molecules. Founded on a solid physical framework, these EoS allow explaining the physical nature of fluids, for instance, hydroden-bonding interactions, chain formation, *etc*. The so-called Statistical Associating Fluid Theory (SAFT) equations are the best examples for this category of EoS. The first version of SAFT-type EoS was introduced by Chapman *et al.* with the use of Wertheim's perturbation theory for taking into account associative interactions between molecules [10], [11]. SAFT is generally expressed as contributions to the residual Helmholtz energy A^{res}, as shown in Eq. (2).

$$A^{res} = (mA^{hs} + A^{chain}) + A^{disp} + A^{assoc} + A^{polar} \tag{2}$$

where A^{hs}, A^{chain}, A^{disp}, A^{assoc}, and A^{polar} is terms respectively accounting for contributions from hard-sphere, chain formation, London attractive interaction, associative interaction, and polar characteristics. Each term is characterized by specific parameters such as segment diameter σ, number of segments *m*, well-depth energy of dispersive energy ε/k, association energy ε^{AB}/k and the association volume K^{AB} (where A and B represent the associating sites), the polar moment (dipole moment μ and quadrupole moment q) and the polar fractions ($mx^{p\mu}$ *and* mx^{pQ}). Since 1989, different versions of SAFT models have been developed and proposed in literature [12 - 15]. The main differences among SAFT-type versions essentially come from either (1) the reference system considered, or (2) the choice of approach to describe repulsive and attractive interactions. The use of SAFT-type equations for thermodynamic behavior of complex fluids, for both pure compounds and mixtures, was successfully shown in many investigations [13], [14].

In addition to the two aforementioned equations, many investigators have also developed the so-called hybrid EoS which are based on a cubic-type EoS plus an association term derived from the Wertheim theory [16], [17]. Among many successful models proposed in the literature, much is focused on the so-called CPA (Cubic Plus Association) equation [18] and the GCA (Group Contribution Associating) equation [19]. To extend the capability of cubic-type EoS for associating molecules, Kontogeorgis *et al.* [18] formulated the CPA equation, which is a combination of SRK with the association term derived from SAFT, as shown in Eq. (3).

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} + \frac{RT}{v}\rho \sum_A \left[\frac{1}{X^A} - \frac{1}{2}\right] \frac{\partial X^A}{\partial \rho} \tag{3}$$

where X^A is molar fraction of the compound not-bonded at site A. The characteristic parameters in Eq. (3) were fitted against vapor pressure and saturated liquid density measured values. Successful applications of this model were demonstrated for mixtures containing light hydrocarbons, water and alcohols [20 - 22].

In the case of predicting transport properties such as viscosity, many thermodynamic models have been proposed with the use of different underlying theories such as kinetic theory [23], [24], corresponding states theory [25], free-volume concept [26], friction theory [27], and among others. These models have been shown to be capable of predicting the viscosity of industrial fluids to a reasonable extent [28]. One of the most prominent models, which has been demonstrated to be capable of predicting the viscosity of complex fluids, is the one founded on the kinetic theory of hard sphere. This equation was firstly presented by Dymond [29] and then refined for practical applications by Assael *et al.* [23], as shown in Eqs. (4) & (5).

$$log\left(\frac{\eta^*}{R_\eta}\right) = \sum_{i=0}^{7} a_{\eta i}\,(V^*)^i \tag{4}$$

$$\eta^* = \frac{16}{5}(2N_A)^{1/3}\left(\frac{\pi}{MRT}\right)^{1/2}\frac{V_m^{2/3}}{R_\eta}\eta \tag{5}$$

where V_m, V_o, M, R, T, R_η and η corresponds to the molar volume, the molar core volume, the molar mass, the universal gas constant, the temperature, the roughness factor, and the dynamic viscosity, respectively. The extension of this scheme was applied to predict the viscosity of different complex fluids (synthetic crude oils, aromatics, *etc*) within an uncertainty of 5% [24], [30].

3. Parameterization techniques

As clearly shown in Figure 1, the application of any thermodynamic model should define their characteristic parameters. This step is called "parameterization". There are four techniques commonly used to parameterize an equation of state or a thermodynamic model. These techniques are mainly classified into regression, corresponding states principle, ab initio calculations, group contribution. The following paragraph will present and discuss briefly these techniques.

Direct regression on experimental data is the safest technique to determine characteristic parameters. The use of the parameters obtained by this technique accurately restores properties which are used for the regression. Nevertheless, the extrapolation of these parameters for other applications strongly depends on the physical framework of the model and also the condition range of the database used for the regression. A difficulty with this approach lies in the fact that parameters are very often regressed against pure experimental data. Therefore, extending these regressed parameters to mixtures could reach a severe deviation in predictive results. To overcome this difficulty, spectroscopic data for associatiion-relating parameters or mixture data can be included in the database used for the regression, as done by von Solms *et al.* [31] or Ferrando *et al.* [32].

Another method for parameterizing cubic-type EoS is the corresponding states one [33 - 35]. This well-known principle is based on using properties at critical points and acentric factors to estimate EoS characteristic parameters. Therefore, this technique allows to capture exactly fluid behavior at the critical point. Bouza *et al.* [36] applied this technique to a SAFT-type equation. Consequently, critical points were well captured, but high deviations were still observed elsewhere. This indicates that the corresponding state principle is not suitable to parameterize molecular equations of state like SAFT. This principle was also applied to the transport property model [37 - 40].

The ab initio (quantum mechanical) calculations were used to parameterize SAFT-type EoS by several research groups [41 - 45]. A drawback when using this technique is that the number of compounds considered is limited due to the fact that the computational expense for molecules under consideration is costly.

Another technique which allows to determination of EoS parameters is the Group Contribution (GC) method. To be able to use this technique, the chemical structure of a molecule considered, or more precisely, its molecular functional groups such as CH_3-, -CH_2-, -NH_2-, -COOH, *etc* must be established. Several GC-based approaches were developed for parameterizing cubic EoS, for instance, the well-known Predictive Soave-Redlich-Kwong model [46], which is a combination of SRK with an activity coefficient approach based on the GC technique used to predict the attractive mixture parameter. Based on the PR EoS framework, Jaubert *et al.* [47] developed a GC scheme to estimate the so-called binary interaction parameter k_{ij}. The working groups of Brignole [48] and Stefanis *et al.* [49] also proposed the GC rules for associating compounds. The so-called GCA EoS, combining the GC scheme developed by Skjold-Jorgensen [50] and Wertheim's theory-based association term, was successfully applied to systems of fatty oil derivatives and pure organic compounds. The application of GC techniques for SAFT-type EoS is generally classified into two approaches, namely, homonuclear GC approach and heteronuclear GC approach. Regarding the homonuclear approach, the groups of Passarello and de Hemptinne proposed the average mixing rules for the three non-associating parameters (ε/k, σ, m) of the original SAFT and PC-SAFT [51], [52]. The polar version of the PC-SAFT combined with the GC approach was successfully applied to alkanes, alcohols, aromatic hydrocabons, oxygenated compounds [53]. Among the heteronuclear GC approaches, the prominent one is the scheme proposed by Lymperiadis *et al.* [54], [55]. This scheme, which relied on SAFT-VR, was successfully applied for pure alkanes, pure alcohols, as well as their mixtures [56]. Recently, the GC technique was also developed for viscosity on the basis of the cubic EoS, presented by Cardona *et al.* [57], and of the free-volume theory model, presented by Jovanovic *et al.* [58], with encouraging results.

4. Fluid characterization approaches

To perform thermophysical property calculations with a thermodynamic model, a description of fluid is indispensable. With regard to petroleum refining applications, ill-defined mixtures are often described through a set of pseudocomponents. According to Khan *et al.* [59], the fluid description has to answer four following questions: (1) "How many components should be used?", (2) "How should pseudocomponents be formed?". (3) "How should fluid characterization parameters be obtained?", and finally (4) "Which mixing rules should be used to calculate pseudo-properties?". The first issue is related to the analysis in terms of composition and property measurements of fluids under investigation. The analytical information obtained for the fluids will decide which approaches can be used to create a set of pseudocomponents. This section will review some of the most commonly used methods for fluid characterization. The information on these methods will be organized in order as follows input data, data treatment, and finally fluid characterization.

4.1. Utilization of distillation curves

In the field of petroleum refining, it is impossible to access a full analysis of molecular components for petroleum mixtures. Therefore, these multi-component fluids are commonly described through a set of pseudocomponents which are also assigned thermophysical properties. The application of the pseudocomponent concept aims at reducing the actual number of molecular components being used in simulation softwares. This results in simplifying the calculation operations with a chosen EoS.

4.1.1. Input data

Conventionally, pseudocomponents are generated from distillation curves [60] which are built up from experiments. Distillation is referred to as a separation technique of liquid mixtures or liquefied gas mixtures into individual components or groups of components (*aka* fractions or cuts termed in the refining field) thanks to the volatility difference between chemical components. The output of this molecular separation normally is a curve showing the relationship between boiling temperature and distilled volume percent. Figure 2 is an example of a distillation curve for crude oil, where the X-axis is cumulative liquid volume percent and the Y-axis boiling temperature.

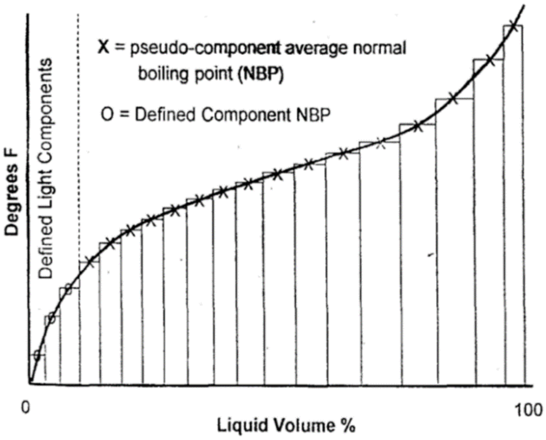

Figure 2. *Typical True Boiling Point curve for a crude oil*

There are different norms for building up distillation curves in the refining industry, for instance, the so-called true-boiling-point (TPB) curve built up according to ASTM D2892 standardized for crude oil, or distillation curves obtained from ASTM D86 standardized for petroleum products, *etc*. Distillation curves can also be obtained by using a gas chromatographic technique (ASTM D2887). These curves are called simulated distillation curves. In practice, obtaining TPB curves is very time-consuming. Therefore, various approaches were developed to obtain these curves from data provided by other norms. Readers are referred to references for more information [61 - 64].

4.1.2. Treatment

As shown in Figure 2, a set of pseudocomponents is generated by cutting the TBP curve of the fluid into different temperature intervals. The smaller the temperature intervals, the more accurate the representation will be. Practically, adequate temperature interval ranges from 10 to 15 degrees Kelvin [65]. Each pseudocomponent defined from the TBP curve is then characterized by an average boiling temperature and density. These properties can be easily and rapidly measured in laboratories. When petroleum fractions cannot be collected and no actual measurement is possible, the density of the fractions is then calculated assuming that the characterization factor K_w [66] is constant throughout the fractions. This factor measures the "paraffinicity" of hydrocarbons. It is defined as the ratio of the cube root of the average boiling point (T_b) and specific gravity (SG) of petroleum fractions, as shown in Eq. (6).

$$K_w = \frac{(1.8T_b)^{1/3}}{SG} \qquad (6)$$

A petroleum fraction behaves as kinds of paraffin if the value of K_w is approximately 13 and as aromatics if K_w is approximately 10.

4.1.3. Characterization

Based on T_b and SG, some properties (*e.g.*, critical temperature and pressure, acentric factor) of the pseudocomponents can be calculated by utilizing adequate correlations, for instance, those proposed by Lee and Kesler [35], but many others can be found in the literature [2], [67].

The fluid characterization as pseudocomponents is widely used as a basic approach in many commercial simulation software like HYSYS, Aspen Plus, Pro/II, *etc* to simulate and design separation processes such as crude oil distillation. The benefits of using this technique lie in the fact that (1) molecular information is not needed; only bulk properties such as T_b and SG are required, and (2) the number of components being simultaneously treated is considerably reduced. Although being able to meet refiners' simulation demands, and being still a prevailing technique in simulating refining processes today, this approach, according to Eckert and Vanëk [68], has some inevitable limitations. Most importantly, this technique is incapable of considering the wealth of complexity in non-petroleum based fluids, for instance, those originating from biomass processing. This is due to the fact that the input information needed for characterization purposes almost exclusively refers to fluid volatility.

4.2. Utilization of lumping approach

Fluids can be characterized by several hypothetical groups by using a lumping technique. By using this technique, components possessing one or a few similar physical properties (*e.g.*, critical temperature and pressure, acentric factor, molecular weight, *etc*) will be lumped or grouped into a hypothetical group.

4.2.1. Input data

Contrary to the above-mentioned the pseudocomponent-based approach, the lumping technique requires a detailed analysis of all fluid components. Thanks to modern analytical instruments such as chromatography, spectroscopy, spectrometry, *etc*, the information on composition (weight or molar percent) and molecular structure for a large range of components in fluids, particularly for petroleum fluids, is accessible. Readers are referred to references [2], [69] for more information. Regarding fluids originating from biomass processing, recent developments in the so-called two-dimensional gas chromatography technique (GC-2D) make it possible to consider oxygenated bio-oils [70], [71]. The description of this modern technique is detailed in some reviews [72], [73].

4.2.2. Treatment

On the basis of detailed molecular information of a fluid under consideration, it is possible to group the fluid components into a limited number of hypothetical components or pseudocomponent. The algorithm proposed by Montel and Gouel [74], also known as the dynamic cloud method, is the most frequently used for lumping purpose. Within this algorithm, several thermophysical properties as input data will be provided for each component together with a corresponding weight factor for each property used. The lumping algorithm will then identify a number of hypothetical groups by minimizing the objective function expressed as d_{ij} (see Eq. (7)). This value is defined as the distance between barycenters (*i.e.*, centers of lumps) of hypothetical groups and the components belonging to these hypothetical groups for all properties considered.

$$d_{ij} = \sum_{k=1}^{n_{properties}} w_k \left| r_{i,k}^2 - r_{j,k}^2 \right| \qquad (7)$$

Where d_{ij} is the distance between compound i and j; w_k is the weighting factor for property k; $r_{i,k}$ is the normalized value of property k of compound i. This value is normalized between the minimum and maximum values of property k of compound i on all the compounds.

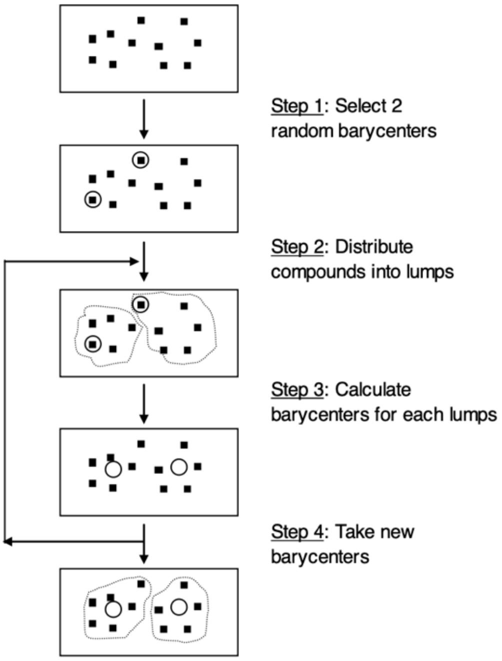

Figure 3. *Algorithm of the lumping scheme [74]*

Basically, the lumping algorithm consists of 4 steps as illustrated in Figure 3. The first step involves random selection of the quantity of lumps and barycenters. In the next step, components are distributed into the lumps based on their nearest distance criterion (see Eq. (7)). Note that the criterion can be one or many properties, as well as specific parameters of an EoS. The barycenters are then determined for each lump based on the distribution procedure done in the second step. In the third step, the distribution of the components will be done iteratively until all barycenters achieve stability, which means that no component moves to another lump [65]. Consequently, the output of this algorithm is a distribution of the initial components in the chosen number of lumps.

4.2.3. Characterization

The properties or EoS specific parameters need determining for each lump. To that end, an averaging rule based on the properties of the lump-belonging components is used. Averaging rules for determining critical properties, molecular weight, and acentric factors for a lump are given as examples in references [74], [75]. As a result, the well-defined lumps can be used as pure components within the framework of the chosen EoS. It should be noted that the lumps generated from this technique can be considered as pseudocomponents in the same way as discussed above. A challenge with using this approach is to identify lumping criteria. That involves the determination of relevant properties used in the objective function.

4.3. Utilization of solvent fractionation approaches

Petroleum fluids, mainly residues, are often characterized by using a solvent-based fractionation approach. The fractionation is achieved due to the variation in terms of solubility and polarity of components of the fluids into different solvents. Basically, this technique utilizes various chemical solvents to fractionate mixtures into different chemical families each of which is treated as a pseudocomponent. A typical illustration of this method is the so-called SARA method which fractionates a crude oil into 4 fractions including Saturates (S), Aromatics (A), Resins (R) and Asphaltenes (A), using solvents including n-heptane, acetone, dimethylformamide [2].

4.3.1. Input data

Various research groups developed their solvent fractionation technique for oxygenated bio-oils originating from biomass processing [76]. Generally, a solvent fractionation strategy for bio-oils involves two steps. Firstly, bio-oils are fractionated by using different solvents. This procedure aims at separating the bio-oils into fractions of different characteristics (*e.g.*, solubility, polarity). The second step of the fractionation strategy involves identifying the chemical composition of the fractionated fractions. The recent developments of modern analytical instruments facilitate the detailed identification of the chemical composition of oil fractions even when only small amounts are available. Chromatographic (both gas and liquid), spectroscopic methods, gas chromatography – mass spectrometry, GC2D – MS or NMR are widely used for fractions obtained from the solvent-based fractionation technique [77]. Several two-step approaches developed for characterizing pyrolysed oils are presented in references [78 - 81].

4.3.2. Treatment

Like the abovementioned SARA method, each fraction obtained from the solvent fractionation approach can be treated as a pseudocomponent.

4.3.3. Characterization

To compute thermodynamic properties with an EoS, it requires the availability of several characteristic parameters (*i.e.*, T_c, P_c, ω) for each of the fractionated fractions. Considering biomass originating fluids, very few of the above-mentioned research groups extend their results to any thermodynamic schemes for property prediction. Therefore, the focus is placed only on examples stemming from the petroleum industry. One of the examples presented in this section is the SARA technique reported by Szewczyk, which is based on the use of a GC method. As reported by Szewczyk [82], a C_{20+} fraction was characterized in terms of four pseudocomponents, namely, saturates, aromatics, resins and asphaltenes. The characteristic parameters of each group were determined by using the GC method developed by Avaullée [83]. Molecular functional groups of each pseudocomponent are identified on the basis of the ^{13}C NMR analysis and molecular weight.

A drawback of using solvent-based fractionation is that it is difficult to obtain reproducible results because the chemical nature of fluids considered, which influences their solubility into solvents, strongly depends upon the origin and processing conditions of the considered fluid. In addition, this technique is very time-consuming and costly.

4.4. Molecular reconstruction of fluids

This section will briefly discuss two approaches, called molecular reconstruction, which are used to generate mixtures that can represent the real mixtures considering the similarity in thermophysical properties. The molecular reconstruction of fluids by using these two approaches allows obtaining detailed insight into fluids of interest such as type of molecules, their composition, *etc*. This valuable information is potentially useful for generating a set of pseudocomponents to represent the fluids for simulation purposes.

4.4.1. Approach proposed by Zhang

Zhang *et al.* developed a technique to estimate molecular composition of petroleum fractions from their bulk properties [84]. Figure 4 shows a general sketch of this technique.

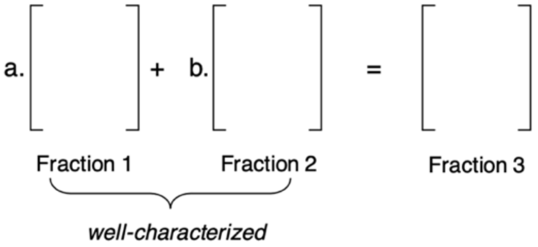

Figure 4. *Approach of Zhang. The "well-characterized" term indicates that the composition matrix of Fraction 1 and 2 is available*

As shown in Figure 4, assuming that Fraction 3 is a mixture of Fraction 1 and Fraction 2 which are well-defined, the molecular composition of Fraction 3 will be then interpolated from the composition of these two fractions. The coefficients a and b as shown in Figure 4 will be adjusted to minimize the deviations between measured properties (*e.g.*, density, refractive index, *etc*) of Fraction 3 and the estimated values. Within the approach proposed by Zhang, the components of the fluids are arranged into a matrix of which the rows represent carbon number and the columns indicate structural groups defined by the author, for instance, three-ring naphthenic compounds, two-ring aromatic compounds, *etc*. Every element of the matrix is the composition (molar or weight percent) of molecules or molecular lumps, for instance, 4A+ lump indicating 4 or 5+ ring aromatic compounds. Table 2 is a typical example of the compositional matrix for a middle distillate. This approach was successfully applied in some cases [85], [86].

Table 2. *Example of the composition representation (%w) in a matrix for a middle distillate. The data are taken from reference [87]*

	P	1N	2N	3N	A	1A1N	1A2N	2A	2A1N	2A2N	3A	4A+
C_9	0.00	0.00	0.00	0.00	0.48	0.18	0.00	0.00	0.00	0.00	0.00	0.00
C_{10}	0.01	0.05	0.00	0.00	0.96	0.37	0.00	0.20	0.00	0.00	0.00	0.00
C_{11}	0.02	0.06	0.00	0.00	1.91	0.74	0.00	0.98	0.00	0.00	0.00	0.00
C_{12}	0.03	0.10	0.05	0.00	1.82	0.70	0.00	1.91	0.00	0.00	0.00	0.00
C_{13}	0.96	0.23	0.14	0.05	1.34	0.52	0.46	4.30	0.76	0.00	0.00	0.00
C_{14}	1.72	0.38	0.24	0.10	0.96	0.51	0.34	6.75	1.59	0.00	0.48	0.00
C_{15}	2.39	0.48	0.57	0.19	0.48	0.38	0.21	5.76	1.36	0.00	1.83	0.00
C_{16}	2.48	0.48	0.48	0.20	0.48	0.35	0.11	4.79	1.14	0.00	1.26	0.06
C_{17}	2.87	0.48	0.29	0.21	0.38	0.19	0.10	4.01	1.02	0.81	1.91	0.28
C_{18}	2.68	0.43	0.29	0.21	0.19	0.14	0.05	1.91	0.45	1.27	1.34	0.25
C_{19}	2.77	0.38	0.29	0.21	0.19	0.14	0.05	0.98	0.23	1.09	0.58	0.39
C_{20}	2.01	0.31	0.24	0.19	0.00	0.08	0.00	0.49	0.19	0.91	0.21	0.28
C_{21}	1.72	0.21	0.19	0.10	0.00	0.05	0.00	0.19	0.11	0.76	0.10	0.14
C_{22}	1.05	0.15	0.14	0.08	0.00	0.00	0.00	0.11	0.07	0.37	0.08	0.13
C_{23}	0.76	0.11	0.10	0.08	0.00	0.00	0.00	0.00	0.05	0.18	0.04	0.11
C_{24}	0.29	0.06	0.05	0.04	0.00	0.00	0.00	0.00	0.02	0.09	0.01	0.06
C_{25}	0.19	0.04	0.00	0.02	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.03
C_{26}	0.10	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00

4.4.2. Approach proposed by Hudebine

Hudebine *et al.* developed an approach, called Entropy Maximization, to characterize petroleum fractions. This approach allows thgeneration of mixtures of molecules of the same behavior as the petroleum fractions under consideration [88], [89] with the use of partial analytical information. This approach consists of two steps. Firstly, a reference mixture as representative as possible of the real fluid is generated by using a stochastic reconstruction method. This reconstruction method is based on the use of a set of random distribution functions of structural blocks such as aromatic rings, naphthenic rings, *etc* or molecular characteristics such as type of molecule, chain length of molecule, probability of presence of functional groups, *etc*. A Monte Carlo sampling method is then applied to generate this reference mixture. It should be noted that the molar fraction of all the molecules in the reference mixture is always normalized to the total number of molecules. Note that the reference mixture may contain several times the same molecule. For each molecule generated, several properties are also determined by using GC-based correlations (*e.g.*, specific gravity, molecular weight, normal boiling point, *etc*). The properties of the reference mixture are averaged by using mixing rules and compared to the measured properties of the real fluid in order to adjust the parameters of the distribution functions. The reference mixture can be composed of several thousands of molecules. For instance, a set of 5000 molecules is generated to represent an Arabian Light vacuum residue [90].

Starting from the reference mixture, the molar fractions of molecules are adjusted by maximizing the entropy of the fluid. The difference between the fluid properties and the measured ones is kept to be as small as possible. If any property value of any molecule is not present in the objective function, the entropy maximization technique will make that molecule not preferred to other molecules. Figure 5 is a typical example of the molar fraction distribution of a mixture of 5000 molecules, representing an Arabian Light vacuum. The molar fraction distribution of the equimolar mixture is uniform.

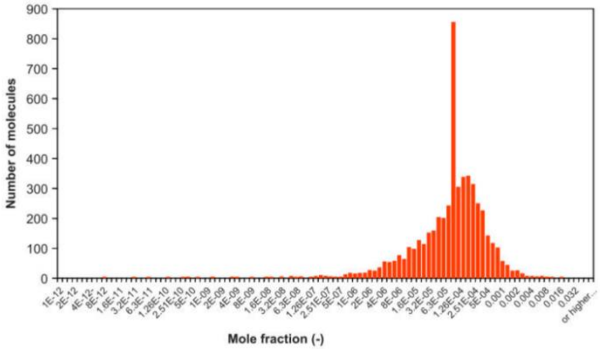

Figure 5. *Distribution of the molar fractions of a mixture representative of an Arabian Light Vacuum residue. This figure is taken from reference [90]*

This approach was applied with encouraging results for reconstructing gasolines and gasoils produced from the fluid catalytic cracking unit, heavy petroleum residue fractions [88], [91], [92], [93]. However, this approach has not yet been extended to oxygenated fluids. In addition, this approach has never been combined with an EoS for phase equilibrium computations. As such, it is probably not adequate because it has to consider a very large number of components. Nevertheless, if combined with a lumping algorithm as mentioned above, this approach could be used as an input so as to generate a number pseudocomponents.

4.5. Concluding remarks

It is proposed in this study a short literature review on how to calculate a thermophysical property of a complex fluid of interest. To that end, an appropriate approach for characterizing the fluid under consideration is indispensible. Table 3 summarizes the approaches which can be served for this purpose.

Nguyen *et al.* [94] proposed a methodology which was successfully used to characterize biodiesel and regular diesel for the thermodynamic property prediction. Based on the aforementioned analysis of fluid characterization approaches, the approach proposed by Nguyen et al. [94] is introduced in this work as a recommendation for an industrially complex fluid characterization. As can be seen in Figure 6, it is possible to calculate properties of a complex fluid provided that an adequate characterization strategy is available. Depending on the type of experimental information obtained for considered fluids, several routes can be used for characterizing a complex fluid. Within the framework of this scheme, the complex fluid will be characterized as pseudocomponents. There are three possible ways to generate pseudocomponents with characteristic parameters depending on the type of availability of analytical information. If an adequate solvent fractionation strategy exists (third arrow), it will be easy to separate complex fluids as fractions with characteristic parameters which are experimentally accessible or predicted by using existing correlations. If a compositionally detailed analysis for complex fluids exists (first arrow) and all thermophysical properties of listed molecules are provided by means of experiments or predictive tools, a lumping strategy can be used to generate pseudocomponents. The characteristic properties of these pseudocomponents can be calculated by using average mixing rules. If there exists only partial analytical information on complex fluids (second arrow), the entropy maximization technique proposed by Hudebine *et al.* can be considered to produce a detailed molecular composition of the fluids. In this case, a lumping strategy is subsequently needed to generate pseudocomponents.

Table 3. *Summary of the characterization methods*

Method	Input data	Treatment	Characterization	Description	Note
TBP	volatility curves	cutting into temperature intervals and attribution of a density to each cut	correlations calculating critical parameters	corresponding states based pseudo-components	only volatilities; use of cubic EoS
Solvent fractionation	set of fractions using selected solvents	each fraction is one pseudo-component	additional measurements are needed, typically to determine the functional groups	use group contribution to construct pseudo-molecules	same global approach as volatility curves except that the criterion is chemical affinity rather than volatility
Lumping	detailed molecular composition	lumping on adequate criteria	mixing rules	pseudo-components characterized by any chosen property	requires detailed information, but potentially to be applied with any model
Molecular reconstruction (Hudebine)	any analytical data	statistical reconstruction	group contribution	large number of molecules	inconvenient to use as such, should be used as an input for lumping

Once pseudocomponents or representative molecules together with their characteristic parameters of complex fluids are generated, one can now use any predictive thermodynamic models for thermophysical property prediction purposes.

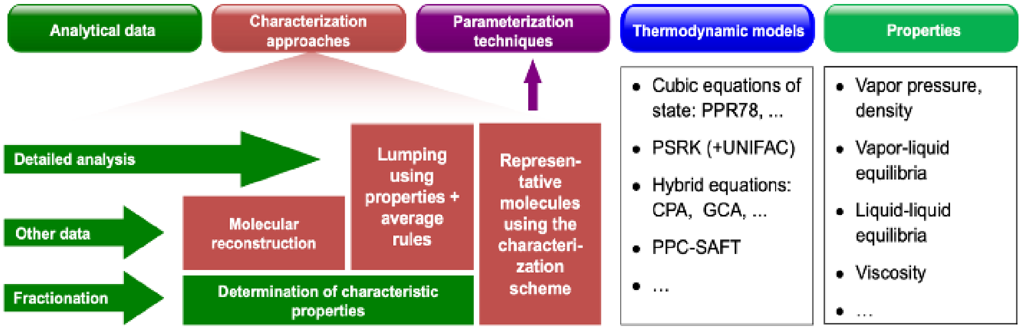

Figure 6. *Proposition of the methodology for characterizing complex fluids (Modified from refrence [94])*

5. Conclusion

The objective of this work is to provide a short review of several approaches which can be applied to computing thermophysical properties of a complex industrial fluid whose composition is very complex and usually unknown. To be able to calculate a property within the scope of a chosen equation of state or a selected thermodynamic model, a fluid characterization is indispensable. The selection of an appropriate method for the characterization purpose strongly depends on the availability of analytical information. Taking advantage of the pseudocomponent concept, a methodology proposed by Nguyen *et al.* is recommended for characterizing complex fluids as a set of representative molecules. These molecules can be then easily applied in any thermodynamic models for computing thermophysical properties. Out of the scope of this work but in the future, a further validation of this methodology for real fluids will be performed.

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REFERENCE

[1] E. Hendriks *et al.*, “Industrial Requirements for Thermodynamics and Transport Properties”, *Ind Eng Chem Res*, vol. 49, no. 22, pp. 11131–11141, Nov. 2010, doi: 10.1021/ie101231b.

[2] M. R. Riazi, *Characterization and Properties of Petroleum Fractions*. Philadelphia: ASTM, 2005.

[3] G. W. Huber, S. Iborra, and A. Corma, “Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering”, *Chem Rev*, vol. 106, no. 9, pp. 4044–4098, Sep. 2006, doi: 10.1021/cr068360d.

[4] D. L. Katz and G. G. Brown, “Vapor Pressure and Vaporization of Petroleum Fractions”, *Ind Eng Chem*, vol. 25, no. 12, pp. 1373–1384, Dec. 1933, doi: 10.1021/ie50288a018.

[5] J. D. Van der Waals, “On the Continuity of the Gaseous and Liquid States”, Universiteit Leiden, Leiden, 1873.

[6] Y. S. Wei and R. J. Sadus, “Equations of state for the calculation of fluid-phase equilibria”, *AIChE Journal*, vol. 46, no. 1, pp. 169–196, Jan. 2000, doi: 10.1002/aic.690460119.

[7] J. O. Valderrama, “The State of the Cubic Equations of State”, *Ind Eng Chem Res*, vol. 42, no. 8, pp. 1603–1618, Apr. 2003, doi: 10.1021/ie020447b.

[8] G. Soave, “Equilibrium constants from a modified Redlich-Kwong equation of state”, *Chem Eng Sci*, vol. 27, no. 6, pp. 1197–1203, Jun. 1972, doi: 10.1016/0009-2509(72)80096-4.

[9] D.-Y. Peng and D. B. Robinson, “A New Two-Constant Equation of State”, *Industrial & Engineering Chemistry Fundamentals*, vol. 15, no. 1, pp. 59–64, Feb. 1976, doi: 10.1021/i160057a011.

[10] W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, “SAFT: Equation-of-state solution model for associating fluids”, *Fluid Phase Equilib*, vol. 52, pp. 31–38, Dec. 1989, doi: 10.1016/0378-3812(89)80308-5.

[11] W. G. Chapman, K. E. Gubbins, G. Jackson, and M. Radosz, “New reference equation of state for associating liquids”, *Ind Eng Chem Res*, vol. 29, no. 8, pp. 1709–1721, Aug. 1990, doi: 10.1021/ie00104a021.

[12] G. M. Kontogeorgis and G. K. Folas, *Thermodynamic Models for Industrial Applications*. Wiley, 2010. doi: 10.1002/9780470747537.

[13] E. A. Müller and K. E. Gubbins, “Molecular-Based Equations of State for Associating Fluids: A Review of SAFT and Related Approaches”, *Ind Eng Chem Res*, vol. 40, no. 10, pp. 2193–2211, May 2001, doi: 10.1021/ie000773w.

[14] I. G. Economou, “Statistical Associating Fluid Theory: A Successful Model for the Calculation of Thermodynamic and Phase Equilibrium Properties of Complex Fluid Mixtures”, *Ind Eng Chem Res*, vol. 41, no. 5, pp. 953–962, Mar. 2002, doi: 10.1021/ie0102201.

[15] S. P. Tan, H. Adidharma, and M. Radosz, “Recent Advances and Applications of Statistical Associating Fluid Theory”, *Ind Eng Chem Res*, vol. 47, no. 21, pp. 8063–8082, Nov. 2008, doi: 10.1021/ie8008764.

[16] M. S. Wertheim, “Fluids of dimerizing hard spheres, and fluid mixtures of hard spheres and dispheres”, *J Chem Phys*, vol. 85, no. 5, pp. 2929–2936, Sep. 1986, doi: 10.1063/1.451002.

[17] M. S. Wertheim, “Fluids with highly directional attractive forces. II. Thermodynamic perturbation theory and integral equations”, *J Stat Phys*, vol. 35, no. 1–2, pp. 35–47, Apr. 1984, doi: 10.1007/BF01017363.

[18] G. M. Kontogeorgis, E. C. Voutsas, I. V Yakoumis, and D. P. Tassios, “An Equation of State for Associating Fluids”, *Ind Eng Chem Res*, vol. 35, no. 11, pp. 4310–4318, Jan. 1996, doi: 10.1021/ie9600203.

[19] H. P. Gros, S. Bottini, and E. A. Brignole, “A group contribution equation of state for associating mixtures”, *Fluid Phase Equilib*, vol. 116, no. 1, pp. 537–544, 1996, doi: https://doi.org/10.1016/0378-3812(95)02928-1.

[20] S. O. Derawi, M. L. Michelsen, G. M. Kontogeorgis, and E. H. Stenby, “Application of the CPA equation of state to glycol/hydrocarbons liquid–liquid equilibria”, *Fluid Phase Equilib*, vol. 209, no. 2, pp. 163–184, 2003, doi: https://doi.org/10.1016/S0378-3812(03)00056-6.

[21] S. O. Derawi, G. M. Kontogeorgis, M. L. Michelsen, and E. H. Stenby, “Extension of the Cubic-Plus-Association Equation of State to Glycol−Water Cross-Associating Systems”, *Ind Eng Chem Res*, vol. 42, no. 7, pp. 1470–1477, Apr. 2003, doi: 10.1021/ie0206103.

[22] I. V Yakoumis, G. M. Kontogeorgis, E. C. Voutsas, and D. P. Tassios, “Vapor-liquid equilibria for alcoholhydrocarbon systems using the CPA Equation of state”, *Fluid Phase Equilib*, vol. 130, no. 1, pp. 31–47, 1997, doi: https://doi.org/10.1016/S0378-3812(96)03200-1.

[23] M. J. Assael, J. H. Dymond, M. Papadaki, and P. M. Patterson, “Correlation and prediction of dense fluid transport coefficients. I. n-alkanes”, *Int J Thermophys*, vol. 13, no. 2, pp. 269–281, 1992.

[24] T.-B. Nguyen, N. Riesco, and V. Vesovic, “Predicting the viscosity of n-alkane liquid mixtures based on molecular description”, *Fuel*, vol. 208, pp. 363–376, 2017.

[25] J. F. Ely and H. J. M. Hanley, “Prediction of Transport Properties of Petroleum Fractions. 1. Viscosity of Fluids and Mixtures”, *Ind. Eng. Chem. Fundamen.*, vol. 20, pp. 323–332, 1981.

[26] A. Allal, C. Boned, and A. Baylaucq, “Free-Volume Viscosity Model for Fluids in the Dense and Gaseous States”, *Phys. Rev. E*, vol. 64, p. 11203, 2001.

[27] S. E. Quinones-Cisneros and U. K. Deiters, “Generalization of the Friction Theory for Viscosity Modeling”, *J. Phys. Chem. B*, vol. 110, pp. 12820–12834, 2006.

[28] W. D. Monnery, W. Y. Svrcek, and A. K. Mehrotra, “Viscosity: A critical review of practical predictive and correlative methods”, *Can J Chem Eng*, vol. 73, no. 1, pp. 3–40, Feb. 1995, doi: https://doi.org/10.1002/cjce.5450730103.

[29] J. H. Dymond, “The interpretation of transport coefficients on the basis of the Van der Waals model. I dense fluids”, *Physica*, vol. 75, no. 1, pp. 100–114, 1974, doi: 10.1016/0031-8914(74)90294-8.

[30] T.-B. Nguyen and V. Vesovic, “Predicting the viscosity of liquid mixtures consisting of n-alkane, alkylbenzene and cycloalkane species based on molecular description”, *Fluid Phase Equilib*, vol. 487, pp. 58–70, 2019.

[31] N. von Solms, M. L. Michelsen, and G. M. Kontogeorgis, “Computational and Physical Performance of a Modified PC-SAFT Equation of State for Highly Asymmetric and Associating Mixtures”, *Ind Eng Chem Res*, vol. 42, no. 5, pp. 1098–1105, Mar. 2003, doi: 10.1021/ie020753p.

[32] N. Ferrando, J.-C. de Hemptinne, P. Mougin, and J.-P. Passarello, “Prediction of the PC-SAFT Associating Parameters by Molecular Simulation”, *J Phys Chem B*, vol. 116, no. 1, pp. 367–377, Jan. 2012, doi: 10.1021/jp209313a.

[33] H. W. Xiang, *The Corresponding-States Principle and its Practice*. Amsterdam: Elsevier, 2005. doi: 10.1016/B978-0-444-52062-3.X5000-3.

[34] T. W. Leland and P. S. Chappelear, "THE CORRESPONDING STATES PRINCIPLE—A REVIEW OF CURRENT THEORY AND PRACTICE", *Ind Eng Chem*, vol. 60, no. 7, pp. 15–43, Jul. 1968, doi: 10.1021/ie50703a005.

[35] B. I. Lee and M. G. Kesler, "A generalized thermodynamic correlation based on three-parameter corresponding states", *AIChE Journal*, vol. 21, no. 3, pp. 510–527, May 1975, doi: https://doi.org/10.1002/aic.690210313.

[36] A. Bouza, C. M. Colina, and C. G. Olivera-Fuentes, "Parameterization of molecular-based equations of state", *Fluid Phase Equilib*, vol. 228–229, pp. 561–575, 2005, doi: https://doi.org/10.1016/j.fluid.2004.08.043.

[37] N. Lindeloff, K. S. Pedersen, H. P. Ronningsen, and J. Milter, "The Corresponding States Viscosity Model Applied to Heavy Oil Systems", *J. Can. Pet. Tech.*, vol. 43, pp. 47–53, 2004.

[38] A. S. Teja and P. Rice, "Generalized Corresponding State Method for the Viscosities of Liquid Mixtures", *Ind. Eng. Chem. Fundamen.*, vol. 20, pp. 77–81, 1981.

[39] A. J. Queimada, L. I. Rolo, A. I. Caco, I. M. Marrucho, E. H. Stenby, and J. A. P. Coutinho, "Prediction of Viscosities and Surface Tensions of Fuels Using a New Corresponding States Model", *Fuel*, vol. 85, pp. 874–877, 2006.

[40] H. M. Moharam and M. A. Fahim, "Prediction of Viscosity of Heavy Petroleum Fractions and Crude Oils Using a Corresponding States Method", *Ind. Eng. Chem. Res.*, vol. 34, pp. 4140–4144, 1995.

[41] M. Singh, K. Leonhard, and K. Lucas, "Making equation of state models predictive: Part 1: Quantum chemical computation of molecular properties", *Fluid Phase Equilib*, vol. 258, no. 1, pp. 16–28, 2007, doi: https://doi.org/10.1016/j.fluid.2007.05.021.

[42] K. Leonhard, N. Van Nhu, and K. Lucas, "Making Equation of State Models Predictive−Part 3: Improved Treatment of Multipolar Interactions in a PC-SAFT Based Equation of State", *The Journal of Physical Chemistry C*, vol. 111, no. 43, pp. 15533–15543, Nov. 2007, doi: 10.1021/jp0726081.

[43] K. Leonhard, N. Van Nhu, and K. Lucas, "Making equation of state models predictive: Part 2: An improved PCP-SAFT equation of state", *Fluid Phase Equilib*, vol. 258, no. 1, pp. 41–50, 2007, doi: https://doi.org/10.1016/j.fluid.2007.05.019.

[44] J. P. Wolbach and S. I. Sandler, "Using Molecular Orbital Calculations To Describe the Phase Behavior of Hydrogen-Bonding Fluids", *Ind Eng Chem Res*, vol. 36, no. 10, pp. 4041–4051, Oct. 1997, doi: 10.1021/ie9607255.

[45] J. P. Wolbach and S. I. Sandler, "Using Molecular Orbital Calculations To Describe the Phase Behavior of Cross-associating Mixtures", *Ind Eng Chem Res*, vol. 37, no. 8, pp. 2917–2928, Aug. 1998, doi: 10.1021/ie970781l.

[46] T. Holderbaum and J. Gmehling, "PSRK: A Group Contribution Equation of State Based on UNIFAC", *Fluid Phase Equilib*, vol. 70, no. 2, pp. 251–265, 1991, doi: https://doi.org/10.1016/0378-3812(91)85038-V.

[47] J.-N. Jaubert and F. Mutelet, "VLE predictions with the Peng–Robinson equation of state and temperature dependent kij calculated through a group contribution method", *Fluid Phase Equilib*, vol. 224, no. 2, pp. 285–304, 2004, doi: https://doi.org/10.1016/j.fluid.2004.06.059.

[48] O. Ferreira, E. A. Macedo, and E. A. Brignole, "Application of the GCA-EoS model to the supercritical processing of fatty oil derivatives", *J Food Eng*, vol. 70, no. 4, pp. 579–587, 2005, doi: https://doi.org/10.1016/j.jfoodeng.2004.10.012.

[49] E. Stefanis, L. Constantinou, I. Tsivintzelis, and C. Panayiotou, "New Group-Contribution Method for Predicting Temperature-Dependent Properties of Pure Organic Compounds", *Int J Thermophys*, vol. 26, no. 5, pp. 1369–1388, 2005, doi: 10.1007/s10765-005-8092-7.

[50] S. Skjold-Joergensen, "Group contribution equation of state (GC-EOS): a predictive method for phase equilibrium computations over wide ranges of temperature and pressures up to 30 MPa", *Ind Eng Chem Res*, vol. 27, no. 1, pp. 110–118, Jan. 1988, doi: 10.1021/ie00073a021.

[51] D. Nguyen-Huynh, J.-C. de Hemptinne, R. Lugo, J.-P. Passarello, and P. Tobaly, "Modeling Liquid–Liquid and Liquid–Vapor Equilibria of Binary Systems Containing Water with an Alkane, an Aromatic Hydrocarbon, an Alcohol or a Gas (Methane, Ethane, CO2 or H2S), Using Group Contribution Polar Perturbed-Chain Statistical Associating Fluid Theory", *Ind Eng Chem Res*, vol. 50, no. 12, pp. 7467–7483, Jun. 2011, doi: 10.1021/ie102045g.

[52] M. S. Tamouza and J. P. Petitet, "Utilisation Prédictive de l'Equation d'Etat SAFT", 2004.

[53] T.-B. Nguyen, J.-C. de Hemptinne, B. Creton, and G. M. Kontogeorgis, "GC-PPC-SAFT Equation of State for VLE and LLE of Hydrocarbons and Oxygenated Compounds. Sensitivity Analysis", *Ind Eng Chem Res*, vol. 52, no. 21, pp. 7014–7029, May 2013, doi: 10.1021/ie3028069.

[54] A. Lymperiadis, C. S. Adjiman, A. Galindo, and G. Jackson, "A group contribution method for associating chain molecules based on the statistical associating fluid theory (SAFT-γ)", *J Chem Phys*, vol. 127, no. 23, p. 234903, Dec. 2007, doi: 10.1063/1.2813894.

[55] A. Lymperiadis, C. S. Adjiman, G. Jackson, and A. Galindo, "A generalisation of the SAFT-γ group contribution method for groups comprising multiple spherical segments", *Fluid Phase Equilib*, vol. 274, no. 1, pp. 85–104, 2008, doi: https://doi.org/10.1016/j.fluid.2008.08.005.

[56] A. Gil-Villegas, A. Galindo, P. J. Whitehead, S. J. Mills, G. Jackson, and A. N. Burgess, "Statistical associating fluid theory for chain molecules with attractive potentials of variable range", *J Chem Phys*, vol. 106, no. 10, pp. 4168–4186, Mar. 1997, doi: 10.1063/1.473101.

[57] L. F. Cardona, L. A. Forero, and J. A. Velásquez, "Extension of a Group Contribution Method to Predict Viscosity Based on Momentum Transport Theory Using a Modified Peng–Robinson EoS", *Ind Eng Chem Res*, vol. 60, no. 41, pp. 14903–14926, Oct. 2021, doi: 10.1021/acs.iecr.1c02146.

[58] J. D. Jovanović, N. D. Grozdanić, I. R. Radović, and M. Lj. Kijevčanin, "A new group contribution model for prediction liquid hydrocarbon viscosity based on free-volume theory", *J Mol Liq*, vol. 376, p. 121452, 2023, doi: https://doi.org/10.1016/j.molliq.2023.121452.

[59] S. A. Khan, G. A. Pope, and K. Sepehrnoori, "Fluid Characterization of Three-Phase CO2/Oil Mixtures", in *All Days*, SPE, Apr. 1992. doi: 10.2118/24130-MS.

[60] M. R. Riazi and Y. A. Roomi, "Potential Approaches Toward Characterization and Property Estimation of Heavy Petroleum Fluids and Natural Gas Systems", *Pet Sci Technol*, vol. 26, no. 18, pp. 2159–2169, Dec. 2008, doi: 10.1080/10916460701429548.

[61] T. E. Daubert, "Petroleum fraction distillation interconversions", *Hydrocarbon Processing; (United States)*, vol. 73, no. 9, 1994, [Online]. Available: https://www.osti.gov/biblio/6781634

[62] M. R. Riazi and T. E. Daubert, "Analytical distillation-curve types correlations interconvert", *Oil & Gas Journal*, 1986, [Online]. Available: https://api.semanticscholar.org/CorpusID:93136293

[63] W. C. Edmister and K. K. Okamoto, "Applied Hydrocarbon Thermodynamics - Part 12: Equilibrium Flash Vaporization Correlation for Petroleum Fractions", *Petroleum Refiner*, vol. 38, no. 8, pp. 117–132, 1959.

[64] E. J. Hoffman, "Relations between true boiling point and ASTM distillation curves", *Chem Eng Sci*, vol. 24, no. 1, pp. 113–117, 1969, doi: https://doi.org/10.1016/0009-2509(69)80013-8.

[65] J.-C. de Hemptinne, J.-M. Ledanois, P. Mougin, and A. Barreau, *Select Thermodynamic Models for Process Simulation - A Practical Guide using a Three Steps Methodology*. Technip, 2012. doi: 10.2516/ifpen/2011001.

[66] K. M. Watson and E. F. Nelson, "Improved Methods for Approximating Critical and Thermal Properties of Petroleum Fractions", *Ind Eng Chem*, vol. 25, no. 8, pp. 880–887, Aug. 1933, doi: 10.1021/ie50284a012.

[67] C. H. Twu, "An internally consistent correlation for predicting the critical properties and molecular weights of petroleum and coal-tar liquids", *Fluid Phase Equilib*, vol. 16, no. 2, pp. 137–150, 1984, doi: https://doi.org/10.1016/0378-3812(84)85027-X.

[68] E. Eckert and T. Vaněk, "New approach to the characterisation of petroleum mixtures used in the modelling of separation processes", *Comput Chem Eng*, vol. 30, no. 2, pp. 343–356, 2005, doi: https://doi.org/10.1016/j.compchemeng.2005.10.005.

[69] J. G. Speight, *The Chemistry and Technology of Petroleum*. CRC Press, 2006. doi: 10.1201/9781420008388.

[70] J. A. Murray, "Qualitative and quantitative approaches in comprehensive two-dimensional gas chromatography", *J Chromatogr A*, vol. 1261, pp. 58–68, 2012, doi: https://doi.org/10.1016/j.chroma.2012.05.012.

[71] B. Omais, J. Crepier, N. Charon, M. Courtiade, A. Quignard, and D. Thiébaut, "Oxygen speciation in upgraded fast pyrolysis bio-oils by comprehensive two-dimensional gas chromatography", *Analyst*, vol. 138, no. 8, pp. 2258–2268, 2013, doi: 10.1039/C2AN35597C.

[72] M. Adahchour, J. Beens, and U. A. Th. Brinkman, "Recent developments in the application of comprehensive two-dimensional gas chromatography", *J Chromatogr A*, vol. 1186, no. 1, pp. 67–108, 2008, doi: https://doi.org/10.1016/j.chroma.2008.01.002.

[73] W. Bertsch, "Two-Dimensional Gas Chromatography. Concepts, Instrumentation, and Applications – Part 1: Fundamentals, Conventional Two-Dimensional Gas Chromatography, Selected Applications", *Journal of High Resolution Chromatography*, vol. 22, no. 12, pp. 647–665, Dec. 1999, doi: https://doi.org/10.1002/(SICI)1521-4168(19991201)22:12<647::AID-JHRC647>3.0.CO;2-V.

[74] F. Montel and P. L. Gouel, "A New Lumping Scheme of Analytical Data for Compositional Studies", in *SPE Annual Technical Conference and Exhibition*, SPE, Sep. 1984. doi: 10.2118/13119-MS.

[75] C. F. Leibovici, "A consistent procedure for the estimation of properties associated to lumped systems", *Fluid Phase Equilib*, vol. 87, no. 2, pp. 189–197, 1993, doi: https://doi.org/10.1016/0378-3812(93)85026-I.

[76] D. Mohan, C. U. Jr. Pittman, and P. H. Steele, "Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review", *Energy & Fuels*, vol. 20, no. 3, pp. 848–889, May 2006, doi: 10.1021/ef0502397.

[77] K. Sipilä, E. Kuoppala, L. Fagernäs, and A. Oasmaa, "Characterization of biomass-based flash pyrolysis oils", *Biomass Bioenergy*, vol. 14, no. 2, pp. 103–113, 1998, doi: https://doi.org/10.1016/S0961-9534(97)10024-1.

[78] R. Maggi and B. Delmon, "Characterization and upgrading of bio-oils produced by rapid thermal processing", *Biomass Bioenergy*, vol. 7, no. 1, pp. 245–249, 1994, doi: https://doi.org/10.1016/0961-9534(94)00062-X.

[79] M. Garcia-Perez, A. Chaala, H. Pakdel, D. Kretschmer, and C. Roy, "Characterization of bio-oils in chemical families", *Biomass Bioenergy*, vol. 31, no. 4, pp. 222–242, 2007, doi: https://doi.org/10.1016/j.biombioe.2006.02.006.

[80] C. Amen-Chen, H. Pakdel, and C. Roy, "Separation of phenols from Eucalyptus wood tar", *Biomass Bioenergy*, vol. 13, no. 1, pp. 25–37, 1997, doi: https://doi.org/10.1016/S0961-9534(97)00021-4.

[81] M. E. da Cunha *et al.*, "Analysis of fractions and bio-oil of sugar cane straw by one-dimensional and two-dimensional gas chromatography with quadrupole mass spectrometry (GC×GC/qMS)", *Microchemical Journal*, vol. 110, pp. 113–119, 2013, doi: https://doi.org/10.1016/j.microc.2013.03.004.

[82] V. Szewczyk and J. Dellacherie, "Modélisation thermodynamique compositionnelle de la floculation des bruts asphalténiques", 1997.

[83] L. Avaullee, L. Trassy, E. Neau, and J. N. Jaubert, "Thermodynamic modeling for petroleum fluids I. Equation of state and group contribution for the estimation of thermodynamic parameters of heavy hydrocarbons", *Fluid Phase Equilib*, vol. 139, no. 1, pp. 155–170, 1997, doi: https://doi.org/10.1016/S0378-3812(97)00168-4.

[84] Y. Zhang, "A Molecular Approach for Characterization and Property Predictions of Petroleum Mixtures with Applications to Refinery Modelling", UMIST, Manchester,UK, 1999.

[85] J. Gomez-Prado, N. Zhang, and C. Theodoropoulos, "Characterisation of heavy petroleum fractions using modified molecular-type homologous series (MTHS) representation", *Energy*, vol. 33, no. 6, pp. 974–987, 2008, doi: https://doi.org/10.1016/j.energy.2007.11.006.

[86] M. Mi Saine Aye and N. Zhang, "A novel methodology in transforming bulk properties of refining streams into molecular information", *Chem Eng Sci*, vol. 60, no. 23, pp. 6702–6717, 2005, doi: https://doi.org/10.1016/j.ces.2005.05.033.

[87] A. Fafet and J. Magne-Drisch, "Analyse quantitative détaillée des distillats moyens par couplage CG/SM. Application à l'étude des schémas réactionnels du procédé d'hydrotraitement", *Rev. Inst. Fr. Pét.*, vol. 50, no. 3, pp. 391–404, May 1995, [Online]. Available: https://doi.org/10.2516/ogst:1995026

[88] D. Hudebine and J. J. Verstraete, "Molecular reconstruction of LCO gasoils from overall petroleum analyses", *Chem Eng Sci*, vol. 59, no. 22, pp. 4755–4763, 2004, doi: https://doi.org/10.1016/j.ces.2004.09.019.

[89] D. Hudebine and J. J. Verstraete, "Reconstruction of Petroleum Feedstocks by Entropy Maximization. Application to FCC Gasolines", *Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles*, vol. 66, no. 3, pp. 437–460, May 2011, [Online]. Available: https://doi.org/10.2516/ogst/2011110

[90] J. J. Verstraete, Ph. Schnongs, H. Dulot, and D. Hudebine, "Molecular reconstruction of heavy petroleum residue fractions", *Chem Eng Sci*, vol. 65, no. 1, pp. 304–312, 2010, doi: https://doi.org/10.1016/j.ces.2009.08.033.

[91] L. Pereira de Oliveira, J. J. Verstraete, and M. Kolb, "A Monte Carlo modeling methodology for the simulation of hydrotreating processes", *Chemical Engineering Journal*, vol. 207–208, pp. 94–102, 2012, doi: https://doi.org/10.1016/j.cej.2012.05.039.

[92] L. P. de Oliveira, A. T. Vazquez, J. J. Verstraete, and M. Kolb, "Molecular Reconstruction of Petroleum Fractions: Application to Vacuum Residues from Different Origins", *Energy & Fuels*, vol. 27, no. 7, pp. 3622–3641, Jul. 2013, doi: 10.1021/ef300768u.

[93] N. Charon-Revellin, H. Dulot, C. López-García, and J. Jose, "Kinetic Modeling of Vacuum Gas Oil Hydrotreatment using a Molecular Reconstruction Approach", *Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles*, vol. 66, no. 3, pp. 479–490, May 2011, [Online]. Available: https://doi.org/10.2516/ogst/2010005

[94] T.-B. Nguyen, J.-C. de Hemptinne, B. Creton, and G. M. Kontogeorgis, "Characterization Scheme for Property Prediction of Fluid Fractions Originating from Biomass", *Energy & Fuels*, vol. 29, no. 11, pp. 7230–7241, Nov. 2015, doi: 10.1021/acs.energyfuels.5b00782.