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VIRTUAL LABORATORY FOR THE DESIGN OF STRUCTURED LIPIDS FROM VEGETABLE OILS RESOURCES

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Abstract. The use of available vegetable oils natural resources for producing improved molecules/mixtures is a promising area in tailor-made lipids. For this, it is necessary a multi-scale modelling of different properties, taking into account the relations between molecular structure and desired properties. This modelling by predictive methods can be coupled with optimization techniques for screening among potential candidates the optimal ones according to the set of end-use properties. The present work shows some aspects of the development of a framework for lipids design using groups-based property prediction models and presents some thermodynamic properties and viscosity of triacylglycerols using Group Contribution Models.

Key-words. Lipids, triacylglycerol, vegetable oils, CAMD, CAMbD, group contribution.

INTRODUCTION

The search for renewable resources in the chemical industry plays is essential for achieving sustainable development. Vegetable oils are renewable lipid-based raw materials. They are already used in food, biofuels, cosmetic, soaps, pharmaceutical and lubricants industry. But new products and applications are sought with tailor-made lipids ⁽¹⁾, which are lipids specially designed for give a desired set of properties or functional behaviour. Despite this incentive, the search for new blends of oils designed for a specific application is still based upon empirical experience rather than upon scientific background ⁽²⁾. Vegetable oils industry can better take advantages from market opportunities if a systematic procedure for search the best mixtures/molecules that match the desired properties is available.

This work presents some steps in the development of a computational framework (Virtual Laboratory) for finding the optimal lipid molecules or mixtures for a given application. It is based on the concept of Computer Aided Product Design (CAPD) that can be divided in two sub-problems: Computer-Aided Molecular Design (CAMD) and Computer-Aided Mixture/blend Design (CAM^bD) ⁽³⁾. CAPD reverse principle is: given a set of desired properties, find the best molecules/mixtures that satisfy the needs. According to Constantinou *et al.* ⁽⁴⁾, the solution of the CAPD reverse problem can find new and stable products minimizing the cost of their development while producing superior products. This approach was successful for applications in others fields: drugs, solvents and refrigerants substitutions, polymers, paints and coatings ⁽⁴⁾. We propose to apply it to the design of tailor-made lipids, mainly triacylglycerol molecules/mixtures with improved chemical, physical, medical, nutritious and subjective properties, identifying the best raw materials for achieving it. For a tailor-made lipids virtual laboratory, CAPD concepts need extension to a multi-level modelling to address all the relevant tailor-made lipids length scales, ranging from fatty acids molecular structures to blends of oils solid – liquid properties.

MULTI-LEVEL MODELLING OF STRUCTURED LIPIDS

Structured lipids are modified triacylglycerol molecules by chemically or enzymatically catalyzed reactions. 95% of vegetable oils content is made of hundreds of different triacylglycerols (TAGs); which are molecules formed by 3 fatty acids sterified in a glycerol backbone. For designing specific TAGs molecules or mixtures with improved properties, factors as the chain length of the three

fatty acids, their relative position and the number and location of double bonds must be considered at the molecule level. At the mixture level, composition and type of oils used need to be treated as optimisation variables. In Figure 1 illustrates a general description of the problem.

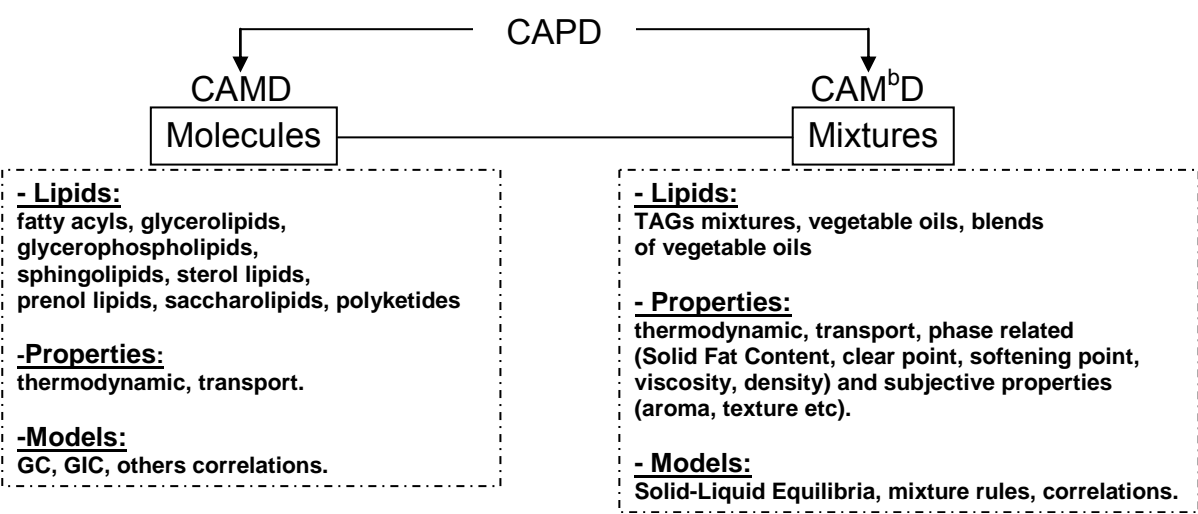


Figure 1: General multi-scale problem representation.

Table 1 summarizes the most important natural higher fatty acids. It highlights the large number of possible molecules; a further motivation for a systematic computational procedure able to search the best candidates that fit the desired properties given by the user.

Table 1: Natural fatty acids.

Carbon Number: Double Bounds	Structure (H3C-(R)-COOH)	Trivial Names	Code
10:0	-[CH ₂] ₈ -	Capric	Dec
12:0	-[CH ₂] ₁₀ -	Lauric	Lau
14:0	-[CH ₂] ₁₂ -	Myristic	Myr
16:0	-[CH ₂] ₁₄ -	Palmitic	Pam
16:1	-[CH ₂] ₅ CH=CH[CH ₂] ₇ -	Palmitoleic	DPam
18:0	-[CH ₂] ₁₆ -	Stearic	Ste
18:1(9)	-[CH ₂] ₇ CH=CH[CH ₂] ₇ -	Oleic	Ole
18:1(11)	-[CH ₂] ₅ CH=CH[CH ₂] ₉ -	Vaccenic	Vac
18:2(9,12)	-[CH ₂] ₃ (CH ₂ CH=CH) ₂ [CH ₂] ₇ -	Linoleic	Lin
18:3(9,12,15)	-(CH ₂ CH=CH) ₃ [CH ₂] ₇ -	(9,12,15)-Linolenic	aLnn
18:3(6,9,12)	-[CH ₂] ₃ (CH ₂ CH=CH) ₃ [CH ₂] ₄ -	(6,9,12)-Linolenic	gLnn
18:3(9,11,13)	-[CH ₂] ₃ (CH=CH) ₃ [CH ₂] ₇ -	Eleostearic	eSte
20:00	-[CH ₂] ₁₈ -	Arachidic	Ach
20:2(8,11)	-[CH ₂] ₆ (CH ₂ CH=CH) ₂ [CH ₂] ₆ -	---	Δ2Ach
20:3(5,8,11)	-[CH ₂] ₆ (CH ₂ CH=CH) ₃ [CH ₂] ₃ -	---	Δ3Ach
20:4(5,8,11,14)	-[CH ₂] ₃ (CH ₂ CH=CH) ₄ [CH ₂] ₃ -	Arachidonic	Δ4Ach
22:0	-[CH ₂] ₂₀ -	Behenic	Beh
24:0	-[CH ₂] ₂₂ -	Lignoceric	Lig
24:1	-[CH ₂] ₇ CH=CH[CH ₂] ₁₃ -	Nervonic	Ner
26:00	[CH ₂] ₂₄ -	Cerotic	Crt
28:0	-[CH ₂] ₂₆ -	Montanic	Mon

STRUCTURED LIPIDS PROPERTIES FOR INDUSTRIAL APPLICATIONS

Figure 2 shows the exponential increase in the number of possible molecules according to the number of fatty acids allowed, taking into account all types of isomers, including optical ones.

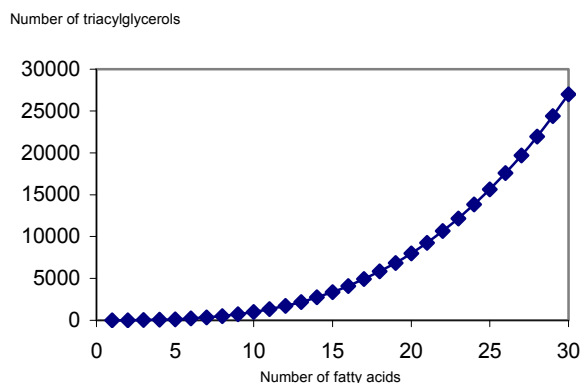


Figure 2: Number of triacylglycerols that can be formed from fatty acids.

Fatty acids type (chain size and double bonds) and position in a TAG structure (Table 1) directly influence thermodynamic and transport properties, solid solubility, crystallization and melting behaviour, solid content, melting profiles, subjective properties and are also related to biochemical reactions in absorption, transport and metabolism of fats in human body ⁽⁵⁾⁽⁶⁾.

In addition to these intramolecular factors, intermolecular issues, in particular polymorphism affects strongly TAGs properties. TAG molecules present basically three different polymorphisms (α , β' , β), each one corresponding to a solid crystalline arrangement ⁽⁷⁾. Differences in molecular packing affect important properties related to crystallization and melting behaviour, such as melting points and enthalpy

of fusion (molecule level), melting ranges and solid content (mixture level) as well as subjective properties related to fat crystal networks in edible products. In fat-based food industry, the quality assessment for some products is attached to a particular desired polymorphism. For example, in margarines, β crystals should be avoided (they cause graininess), in other hand β polymorphism is desired in chocolate production ⁽¹⁾. The polymorphisms dependent thermal properties play a very important role in quality of edible products and directly influence melting behaviour and related perception of texture ⁽⁸⁾. Many subjective and functional properties can also be related to these properties: like texture, creaminess, flavour release, graininess and spreadability.

PROPERTY MODELS

Group Contribution Models (GC)

Group Contribution Methods are predictive properties models ⁽⁹⁾ well suited for CAPD problems provided that they are correlated to data relevant to the problem. Basically, for a given property, a set of known experimental data for different molecules is used to determine correlations where the parameters are the contribution of each chemical group present in the molecule. The equation (1) represents the general equation for property estimations methods using up to third-order groups ⁽⁹⁾:

$$f(X) = \sum_i N_i C_i + w \sum_j M_j D_j + z \sum_k O_k E_k \quad (1)$$

where N, M and O are the number of times a first, second or third order group, respectively, appears in the molecule, C, D and E are the contributions for the property and w and z are binary (0,1) variables used to include or not second and third order groups (respectively).

In this work, the GC method of ⁽⁹⁾ is used for computing the normal boiling point (T_b), critical properties (T_c, V_c, P_c), standard Gibbs energy at 298 K (ΔG_f°), standard enthalpy of formation at 298 K (ΔH_f°) and standard enthalpy of vaporization at 298 K (ΔH_v°). The groups from ⁽⁹⁾ used to represent any type of triacylglycerols are given in Table 2. The type and number of these groups in TAGs vary according to TAG size and chain unsaturations and are automatically managed in the virtual laboratory.

Table 2: Groups used to model Triacylglycerols molecules.

Group	Order
CH ₃	First
CH ₂	First
CH	First
CH=CH	First
CH ₂ COO	First
CH ₂ -CH _m =CH _n (m,n in 0...2)	Second
COO-CH _n -CH _m -OOC (n,m in 1,2)	Second

Group Interaction Contribution Models (GIC)

To take into account isomerism, well acquainted in TAGs, Group Interaction Contribution Models (GIC) are also used in the virtual laboratory development, since the interactions parameters for a given group is available. If there are no available parameters for a chain interaction, models by ⁽¹⁰⁾ can also cope with isomers and symmetry in molecules.

An improved GIC model was presented by ⁽¹¹⁾, and it is used for computing temperature and enthalpy of fusion. This model is based on the following equations:

$$T_m = K_{T,JK} \left(\sum_{IJ} T_{IJ} \right) \quad (2)$$

$$\Delta H_m = K_{H,JK} \left(\sum_{IJ} H_{IJ} \right) \quad (3)$$

Where K is a parameter related to the type of TAG according to the fatty acid repartition (III, IJJ, IJI or IJK) and T_{ij} and H_{ij} are group interaction parameters for temperature and enthalpy of fusion respectively.

RESULTS

Table 3 shows some results for thermodynamic properties calculated using the GC method presented in Equation 1. The virtual laboratory is able to cope with more than 15,600 different TAGs.

Table 3: Thermodynamic properties of triacylglycerols (GC Method).

TAG molecule	T _c (K)	P _c (bar)	V _c (cm ³ /mol)	ΔG _f (kJ/mol)	ΔH _f (kJ/mol)	ΔH _v (kJ/mol)	T _b (K)
StePamMyr	1017.47	7.54	2951.99	- 579.84	- 2067.56	287.36	830.48
LauCrtPam	1039.12	7.27	3289.67	- 531.45	- 2192.53	316.82	852.22
PamLigPam	1045.91	7.19	3402.23	- 515.33	- 2234.19	326.64	859.02
BehCrtBeh	1088.56	6.81	4190.15	- 402.43	- 2525.80	395.38	901.55
AchSteLau	1024.92	7.44	3064.55	- 563.71	- 2109.22	297.18	837.97
AchVacPam	1040.31	7.27	3275.82	- 452.91	- 2078.31	316.34	852.34
PamLinPam	1027.44	7.46	3036.85	- 406.63	- 1880.78	296.21	838.21
OleOleOle	1042.67	7.29	3248.12	- 295.83	- 1849.88	315.37	852.57
MyrOlePam	1018.78	7.55	2938.14	- 501.30	- 1953.34	286.88	830.61
LigOleLau	1040.31	7.27	3275.82	- 452.91	- 2078.31	316.34	852.34

Knowledge of these fundamental properties through the virtual laboratory environment avoids experimental works in the earlier stages of finding new molecules or mixture for a given application, especially when there is a large possibility of combining the fatty acids on the glycerol backbone. Besides, GC methods enable to evaluate molecules for which thermodynamic experimental data is not available. At some latter step within the CAMD framework, experimental data acquisition will then be made on the sole valid candidate molecules.

Thermal Properties

Table 4 shows the ability of GIC models to cope with isomers. Data for three pairs of isomers in each polymorphisms are showed to illustrate the computing results using the model of ⁽¹¹⁾, which show and absolute average deviation of 0.36 % for melting points and 2.17 % for enthalpy of fusion.

Table 4: Fusion enthalpy and temperature of triacylglycerols (GIC Method).

TAG molecule	α	β'	β''
ΔH fus (kJ/mol)			
StePamMyr	89.59	116.10	141.07
PamSteMyr	94.42	135.71	130.52
LauPamLau	79.56	125.57	142.15
PamLauLau	65.10	90.00	115.17
MyrSteLau	71.48	100.23	108.46
SteMyrLau	81.61	93.21	127.86
T fus (K)			
StePamMyr	315.01	330.53	332.26
PamSteMyr	312.48	331.96	331.69
LauPamLau	292.64	315.36	319.48
PamLauLau	295.36	314.87	318.77
MyrSteLau	299.21	320.05	322.80
SteMyrLau	304.41	322.71	324.49

Viscosity

Fats show a complex rheological behaviour due to a mixture of solid crystalline and liquid oil. They have a pseudoplastic behaviour: they look like a solid but can be made to flow by an external force. Under small stresses elastic and viscoelastic deformations occur; under larger stress, yielding and flow occur ⁽¹²⁾. Prediction of pure molecules viscosity gives an understanding of relations between fatty acids structure and viscosity, highlighting the CAMD/CAMbD search procedure.

Rheological properties influence many functional and subjective properties related to fat-based edible products. They can indeed impact flavour perception ⁽¹³⁾.

To predict the viscosity for pure triacylglycerol molecules, the present work uses the group contribution method of ⁽¹⁴⁾ and some results are presented in Figure 3. The viscosity of 5 TAGs vs temperatures is used to illustrate some structure-property relationships. Comparing the molecules, it can be observed that double bounds have a major influence in viscosity. The linoleic acid – based TAG (LinLinLin), despite its bigger chain (18 C) shows the lowest viscosity, due to its higher degree of unsaturation. For TAGs with the same size of fatty acids chain, the higher the number of double bounds, the lower the viscosity.

Although these relations are known, the virtual laboratory gives quantitative data for this structure-property relationship. It also gives a predictive capacity for molecules where no experimental data exist or are difficult to measure.

In Figure 3, the lower temperature used ($T = 400$ K) was kept above the melting point of β modification for all TAGs, to ensure that all phases are liquid, as β polymorphism has the highest melting points among the polymorphisms.

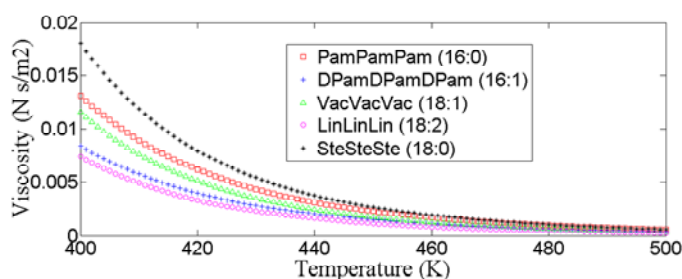


Figure 3: Viscosity of pure triacylglycerols vs. temperature in liquid state.

In general, natural unsaturated fatty acids contain *cis* double bounds. These bonds produces a bend in the straight carbon chain ⁽²⁾ that leads to changes in the way molecules are packing together, reducing temperature of fusion and viscosity. Generation of *trans* double bounds are often related to industrial process of vegetable oils.

CONCLUSIONS

Property prediction is an essential step in the implementation of a Computer Aided Molecular and Mixture Design framework in lipids systems. Group contribution methods can give a predictive capacity for properties needed for modelling structured lipids. They allow insights of how molecular structure affects thermodynamic properties and allow a further investigation for subjective and functional properties of fat-based products. For properties related to crystalline structure, interaction between groups and polymorphisms must be taken into account to a better accuracy in results.

A predictive capacity for different types of properties is also useful in the design, operation and optimization of unit processes, as distillation, heat exchangers, piping and reactors in vegetable oils industry, in a Computer Aided Process Design context.

Besides its use in edible products production, the development of the present framework has also a potential usefulness for other industries that use lipid-based raw materials, like cosmetic, pharmaceuticals, lubricants and biofuels.

The move towards the molecular level for product design is a major trend and challenge for Process System Engineering (PSE) in the future ⁽¹⁵⁾. Development of predictive capabilities for properties of compounds and mixtures and generation of alternatives in order to apply optimization methodologies developed previously for decisions in process design are needed. We propose that the use of renewable materials as vegetable oils is well suited for this structured molecular approach by using Computer Aided Molecular and Mixture Designs techniques according to this PSE Process and Product Design topic.

Further implementation of mixture property models to be coupled with optimization techniques able to find the best candidate molecular structures/mixtures for structured lipids design development.

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