IMPROVEMENT OF PREDICTIVETOOLS OF VAPOR-
LIQUID EQUILIBRIUM BASED ON GROUP CONTRIBUTION
METHODS APPLIED TO LIPID TECHNOLOGY

Daniela S. Damaceno¹

Supervisors: Roberta Ceriani¹ and Rafiqul Gani²

¹ Department of Process and Product Design, University of Campinas
² KT Consortium, Department of Chemical and Biochemical Engineering, Technical University of Denmark
Outline

- Motivation
- Goals
- Work from Brazil and Denmark
- Results
- Conclusions
- Futures steps
Motivation

Vegetable oils world production (USDA, 2017)

Lipids

Million metric ton

0 20 40 60 80 100 120 140 160 180 200

Motivation

Biodiesel world consumption and price (OECD-FAO, 2016)

Consumption (million L)
Price (USD/t)

biodiesel consumption - ↑ 20%
Motivation

1900-2013 = 4,475 data points*

2014-2016 = 1,522 data points*

1900-2013 = 4,475 data points*

*Includes short chain fatty compounds, multi and pseudo compounds

VLE

Experimental data

Oils and fats

KT Consortium Meeting 2017
Motivation

Computer aided tool
Modeling
Experimental data

Predictive models: UNIFAC

Process Design

xi, yi, T, P of pure compounds or mixtures
Goals

**Computer aided tool**

**Modeling**

**Experimental data**

**Experimental (UNICAMP)**
- TPx data, PV
- **DSC** (Differential Scanning Calorimetry),
- **MAG**, **DAG**, ester, alcohol, n-paraffin,
- Subatmospheric pressure
- Wilson, NRTL, UNIQUAC, UNIFACs.

**Modeling (DTU)**
- SPEED Lipid data bank
- **Linear** UNIFAC
- **Dortmund** UNIFAC
- Regress ($a_{nm}$)
- Validation (MoT)
- Original, Linear and Dortmund
Work from Brazil - UNICAMP
Work from Brazil - UNICAMP

CH2
Work from Brazil - UNICAMP
Work from Brazil - UNICAMP
Work from Brazil - UNICAMP
Work from Brazil - UNICAMP

Diverse and new data set
Work from Brazil - UNICAMP

Procedure

- **Ebulliometer**
  - 10 up to 30mL
  - 6 up to 8h

- **DSC**
  - $\pm 5 \, \mu L$
  - Lower cost
  - Reduced time

Work from Brazil - UNICAMP

Binary mixtures → Calibration DSC → Sample preparation → Subatmospheric pressure → Press play and run → Endotherms
Work from Brazil - UNICAMP

Binary mixtures → Calibration DSC → Sample preparation → Subatmospheric pressure → Press play and run → Endotherms
Work from Brazil - UNICAMP

Binary mixtures → Calibration DSC → Sample preparation → Subatmospheric pressure → Press play and run → Endotherms
Work from Brazil - UNICAMP

Binary mixtures → Calibration DSC → Sample preparation → Subatmospheric pressure → Press play and run → Endotherms
Work from Brazil - UNICAMP

Binary mixtures ➔ Calibration DSC ➔ Sample preparation ➔ Subatmospheric pressure ➔ Press play and run ➔ Endotherms
Work from Brazil - UNICAMP

Calculation, modeling and prediction

Binary mixtures → Calibration DSC → Sample preparation → Subatmospheric pressure → Press play and run → Endotherms
Work at DTU

Databank
Evaluation and Regression
Validation

Linear UNIFAC and Dortmund UNIFAC

Weidlich and Gmehling et al., 1987
Work at DTU

\[
\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T}{T}\right)
\]

\[
\psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T}{T}\right)
\]

\[
\phi_i = \frac{r_i^{1/4}}{\sum_j x_j r_j^{1/4}}
\]

---

CH3OH  CH2
CH=CH  OH
CH2CO  CCOO
COOH  H2O
GLY  OHacyl

Linear UNIFAC

Dortmund UNIFAC

Weidlich and Gmehling et al., 1987
Work at DTU

- 330 pure compounds
- 180 data sets
- > 1881 data points

SPEED Lipids database

Perederic et al., 2017 methodology
Work at DTU

I. Data collection and analysis

Step 1. Data collection

Step 2. Data check

Step 3. Data quality screening/testing

II. Data organizing and selection

Step 4. Compounds groups definition and assignment

Step 5. Data category assignment and quality sort

Step 6. Data selection

Systematic Property Modelling

Input information / Required actions and tools

- Literature search
- Database search
- Laboratory measurements
- Check for outliers, pure compound data availability, and transcript errors
- Perform consistency tests: TDE (NIST)
- Groups definition
- Compounds groups assignment
- Algorithm to organize data into categories according to parameter interaction and quality (Algorithm A)
- Algorithm for data selection according to quality factor (Algorithm B)

Output information / Results

- Specific database for the problem is set up
- Refined data
- Consistency test results for the data available
- Representation of each compound involved by constitutive groups and their frequency
- Category-groups with data sets having the same interaction parameters
- Best data sets are selected for parameter estimation

Perederic et al., 2017
Work at DTU

- Understand the **effect on the predictive capacity** of the UNIFAC
- Effect of variations in **each binary interaction** parameter \((a_{mn} \text{ and } b_{mn})\)

III. Parameter estimation and validation

- **MoT**
  - Use original Unifac values or initial estimates
- Use results from organizing algorithm and sensitivity analysis
- Regression tool

- **Step 7. Parameter sensitivity analysis**
  - Most sensitive parameters are identified
- **Step 8. Calculation sequence identification**
  - Order for binary interaction pairs estimation is identified
- **Step 9. Parameter regression**
  - New values for the binary interaction pairs

Perederic et al., 2017
Work at DTU

Step 10. Parameter validation

• Data not used for estimation (rejected in selection step)
• Multicomponent data
• MoT / PRO II

End

New binary interaction pairs are tested on different type of data

Evaluation and Regression

Databank

Validation

Perederic et al., 2017
Work at DTU

- Databank
- Evaluation and Regression
- Validation

Databank from LPT – UNICAMP

Extra data
Results - Experimental

Fatty acid + MAG*

MAG + MAG*

*unpublished data
Results - Experimental

Alcohol + MAG*

*unpublished data
Results - Validation

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Original</th>
<th>Lipids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester + Fatty acid</td>
<td>0.41</td>
<td>0.23</td>
</tr>
<tr>
<td>Alcohols + esters</td>
<td>0.89</td>
<td>0.25</td>
</tr>
<tr>
<td>Unsaturated ester + ester</td>
<td>0.33</td>
<td>0.38</td>
</tr>
<tr>
<td>Ester + ester</td>
<td>1.62</td>
<td>1.62</td>
</tr>
<tr>
<td>Unsaturated fatty acid + fatty acid</td>
<td>0.76</td>
<td>0.79</td>
</tr>
<tr>
<td>Fatty acid + fatty acid</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td>TAG + TAG</td>
<td>1.89</td>
<td>1.87</td>
</tr>
<tr>
<td>MAG + MAG</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>MAG + TAG</td>
<td>0.32</td>
<td>0.18</td>
</tr>
<tr>
<td>DAG + hydrocarbon</td>
<td>0.49</td>
<td>0.44</td>
</tr>
<tr>
<td>Glycerol + Water</td>
<td>2.53</td>
<td>1.09</td>
</tr>
<tr>
<td>Glycerol + alcohol</td>
<td>2.50</td>
<td>1.78</td>
</tr>
</tbody>
</table>

*unpublished data
Results - Validation

<table>
<thead>
<tr>
<th></th>
<th>Original</th>
<th>Lipids</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-paraffin + methanol</td>
<td>1.52</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Improvement
Application

Experimental

Modeling

Computer aided tools

KT Consortium Meeting 2017
Conclusion and future steps

- SPEED Lipids database – over **330 compounds and 180 datasets** to VLE,
- Improvement of Linear and Dortmund UNIFAC for Lipid systems (CH2, COOH, CH2COO, CH2OH, OH, ..)
- Addition of a special groups (GLY) and (OH → acylglycerols),
- Compare differents UNIFACs (T dependence),
- Apply this work to **Product and Process Design**.
THANK YOU