MOLECULAR SOLVENT DESIGN AND NEAR CRITICAL SOLVENTS
OPTIMIZATION WITH ECOFAC

M. CISMONDI, M. S. DIAZ, S. ESPINOSA and E. A. BRIGNOLE

Abstract—In this work an efficient analysis tool for separation process design and property predictions is presented. ECOFAC can estimate pure compound and solution properties, specially some of environmental interest, generate the best potential solvents for a specific liquid-liquid extraction or extractive distillation problem through molecular design, or find the optimal operating conditions for a given supercritical extraction process.

Keywords—Separation Processes, Solvents, Molecular Design, ECOFAC, Supercritical.

I. INTRODUCTION
The computer aided solvent design problem requires different methodologies for liquid solvents and for near critical or supercritical solvents. In the liquid solvents problem there is a great universe of solvent candidates and their selection and evaluation should be made in an efficient way. When dealing with near critical solvents, the solvent choices are few but the operating conditions for its application should be optimized. The use of the same group contribution methods for both property predictions and rigorous process simulation gives also a wide applicability to the computer aided solvent design.

The selection of a liquid solvent can be made testing promising solvent candidates obtained by inspection of component data bases or the properties can be specified and solvent candidates that meet the required properties are generated by molecular design. This is known as the inverse solvent selection problem (Gani and Brignole, 1983) and requires the use of group contribution methods based on UNIFAC or similar group definitions for the prediction of solution properties. The inverse problem has found applications in a great number of product design problems, however the stability of the generated compounds and the quality of the physical property predictions based on group contribution methods have been overlooked in most cases. Pretel et al. (1994) proposed three basic types of group valences, with increasing degree of electronegativity for the feasibility analysis of linear structures. However, this characterization of the group combination properties failed when applied to branched as opposed to linear molecular structures (Cismondi and Brignole, 2001)

On the other hand, chemical processes with supercritical fluids have received increasing interest during the past decade. Experimental data are scarce and difficult to obtain and there is still much research to be done on near critical fluid property prediction, rigorous unit simulations and synthesis and optimum design of these processes (Diaz et al., 2000a).

In this work we present ECOFAC, a set of computer libraries based on group contribution methods for process and property prediction calculations.

II. LIQUID SOLVENTS
The solvent molecular design that ECOFAC performs in a Liquid-liquid extraction or Extractive Distillation problem is based on an upgraded version of the program MOLDES (Pretel et al., 1994). The molecular synthesis has been extended to branched solvent structures with the introduction of new feasibility criteria and rules. In addition, a new characterization of group combination properties had to be made (Cismondi and Brignole, 2001). The formulation of robust feasibility criteria for the synthesis of the branched structures requires in some cases not only the characterization of the group free attachments but also of its internal bonds. When the internal and free bonds are taken into account, only two bond status: K (electronegative) and J (neutral) are required to define the combination properties. The revision of UNIFAC group combination properties is presented in Table 1.

The new synthesis concept is: each J group cannot be attached to more than one K group and the associated feasibility criteria obtained (Cismondi and Brignole, 2001) are shown in Table 2.

The larger number of free attachments (NFA) of the branched intermediate structures greatly increases the size of the synthesis problem in comparison to the synthesis of linear structures. To reduce the problem size, an efficient algorithm based on the concept of metha groups (groups with equivalent combination properties) has been implemented. The ECOFAC computer program executes the following steps:
1. Definition of the desired product property constraints and performance index;
2. Selection of the set of intermediate and terminal groups in an interactive way;
3. Synthesis of feasible metha- Intermediate Molecu-
Table 1. Revision of the combination properties of UNIFAC groups

<table>
<thead>
<tr>
<th>Combination Properties</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M,1)</td>
<td>(CH₃)</td>
</tr>
<tr>
<td>(J,2)</td>
<td>(CH₂)</td>
</tr>
<tr>
<td>(J,3)</td>
<td>(CH)</td>
</tr>
<tr>
<td>(J,4)</td>
<td>(C)</td>
</tr>
<tr>
<td>(J,2) (K,1)</td>
<td>(CH₂Cl)</td>
</tr>
<tr>
<td>(J,3) (K,1)</td>
<td>(CH₂Cl)</td>
</tr>
<tr>
<td>(J,4) (K,1)</td>
<td>(Cl)</td>
</tr>
<tr>
<td>(J,2) (K,2)</td>
<td>(CH₂CO)</td>
</tr>
<tr>
<td>(J,3) (K,2)</td>
<td>(CH₂CO)</td>
</tr>
<tr>
<td>(J,4) (K,2)</td>
<td>(CF)</td>
</tr>
<tr>
<td>(J,3) (K,3)</td>
<td>(CH₃N)</td>
</tr>
<tr>
<td>(J,2) (K,3)</td>
<td>(CH₃N)</td>
</tr>
<tr>
<td>(K,1)</td>
<td>(CH₂=CH)</td>
</tr>
<tr>
<td>(K,2)</td>
<td>(CH=CH)</td>
</tr>
<tr>
<td>(K,3)</td>
<td>(CH=C)</td>
</tr>
<tr>
<td>(K,4)</td>
<td>(C≡C)</td>
</tr>
<tr>
<td>(H,1)</td>
<td>(ACCH₃)</td>
</tr>
<tr>
<td>(H,1)</td>
<td>(ACCH₃)</td>
</tr>
<tr>
<td>(K,1) (H,1)</td>
<td>(AC)</td>
</tr>
<tr>
<td>(J,2) (K,1) (H,1)</td>
<td>(ACCH₃)</td>
</tr>
<tr>
<td>(J,3) (K,1) (H,1)</td>
<td>(ACCH₃)</td>
</tr>
</tbody>
</table>

Table 2. General feasibility criteria for molecular structures

<table>
<thead>
<tr>
<th>Criteria</th>
<th>K ≤ NJF</th>
<th>K &gt; NJF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non cyclic structures</td>
<td>K ≤ J</td>
<td>≥ 2 K ≤ J + NJF</td>
</tr>
<tr>
<td>Cyclic structures</td>
<td>K ≤ J</td>
<td>≥ 2 K ≤ J + NJF</td>
</tr>
<tr>
<td>J = 0</td>
<td>--------</td>
<td>K ≤ 1</td>
</tr>
</tbody>
</table>

The remaining products are ranked in accordance with molecular complexity and performance index, indicating the predicted product properties.

It should be pointed out that between steps 3-4, 4-5, and 6-7 the synthesis procedure eliminates all intermediate and final structures with unknown binary interaction parameters, reducing in this way the size of the combinatorial problem and the computing time. In any case the synthesis program runs in a very short time in a standard PC, as is shown in the example of Tables 3 and 4 for separation of benzene from hexane, which runs in less than one minute.

Table 3. A case of solvent design: separation of benzene from hexane.

<table>
<thead>
<tr>
<th>Problem Definition</th>
<th>Component to be recovered</th>
<th>Principal comp. in raffinate</th>
<th>Separation type</th>
<th>Operation temperature</th>
<th>Interim. groups selected</th>
<th>Terminal groups selected</th>
<th>Problem constraints</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ACH) 6</td>
<td>(CH₃) 2 (CH₃) 4</td>
<td>L-L Extraction</td>
<td>320 K</td>
<td>(C) (CH₃) (CH₂) (DMF-2)</td>
<td>(CH₃) (CH₃=CH) (OH)</td>
<td>Minimum Selectivity [wt] 1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maximum Solvent Loss [wt %] 8.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Minimum Selectivity [wt] 6.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Minimum Solvent Power [wt %] 20.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maximum Solvent Loss [wt %] 4.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Minimum Distribution Coefficient [wt] 0.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maximum Molecular Weight 260.0</td>
</tr>
</tbody>
</table>
III. NEAR CRITICAL SOLVENTS

Each specific supercritical fluid process must be analyzed as a special case in detail. Different processes such as oxychemicals recovery and dehydration from aqueous solutions (Gros et al., 1998; Diaz et al., 2000b), gas antisolvent crystallization (Amaro et al., 2000), separation of fatty acid alkyl esters (Diaz et al., 2000b), vegetable oil purification (Espinosa et al., 2000), and fractionation of fish oil fatty acid ethyl esters (Espinosa et al., 2000c) have been studied in our group with ECOFAC.

ECOFAC describes the high-pressure phase equilibrium behavior with the GCA-EOS model. The original GC-EOS model (Skjold-Jorgensen, 1988) was proposed to study gas solubilities in nonideal mixtures at high pressures and takes into account only repulsive and dispersive interactions. Its capability has been extended (Gros et al., 1997) to treat associating systems in mixtures of water and alcohols with non polar gases, like propane or CO₂. An upgraded version of the GCA-EOS model has been developed for the correlation and simulation of vegetable oils and derivatives processing with near critical fluids (Bottini et al., 1999).

The determination of operating conditions for different supercritical processes are solved as Nonlinear Programming (NLP) problems. Equality constraints represent the process mathematical model and they are solved within a sequential process simulator. This program includes rigorous models for a high-pressure multitstage extractor (Kehat and Ghitis, 1981), low and high-pressure distillation columns (Naphtal and Sandholm, 1971), and a multiphase flash (Michelsen, 1982). Inequality constraints include process specifications, operating bounds and bounds on potential units.

The optimization program interacts with a rigorous sequential modular process simulator in a black box way and non-linear programming problems are solved with OPT (Biegler and Cuthrell, 1985).

Some examples of “solvent design” for supercritical process are given below. Figure 1 shows an example of removal of pollutants from Palm Kernel oil, using propane as a near critical solvent. The results clearly indicate that there is an optimum operating pressure that minimizes solvent requirement keeping the solvent loss below the maximum value (Espinosa et al., 2000a).

The optimum conditions for the operation (counter-current and with reflux) for a destriction (high pressure distillation with a near critical gas as an entrainer) for the deterpenation of citrus oils are presented in Table 5 (Espinosa et al., 2000b).

Table 5: Optimal operating conditions for countercurrent extraction with external reflux.

<table>
<thead>
<tr>
<th>Variable</th>
<th>NLP Optimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractor Pressure (bar)</td>
<td>95.00</td>
</tr>
<tr>
<td>Extractor Temperature (K)</td>
<td>333.15</td>
</tr>
<tr>
<td>Separator Temperature (K)</td>
<td>273.15</td>
</tr>
<tr>
<td>Reflux Ratio</td>
<td>0.54</td>
</tr>
<tr>
<td>Solvent Flowrate (Kmol/h)</td>
<td>82.45</td>
</tr>
<tr>
<td>Linalool in Raffinate, CO₂ free (%molar)</td>
<td>99.00</td>
</tr>
<tr>
<td>Linalool Recovery (%)</td>
<td>93.37</td>
</tr>
<tr>
<td>Limonene in Sep. Bottom (%molar)</td>
<td>98.52</td>
</tr>
<tr>
<td>Limonene Recovery (%)</td>
<td>97.65</td>
</tr>
<tr>
<td>CO₂ in Sep. Vapor (% molar)</td>
<td>99.99</td>
</tr>
</tbody>
</table>
In this case the optimum pressure is a compromise between solvent power of the near critical gas and the operation in the two phase region required to make possible the separation.

**Fig. 1.** Effect of operating pressure on the Propane-feed weight ratio and oil loss in the removal of hexane from palm kernel oil at 390.15 330.15 K (1 wt % of hexane in feed; 5 ppm of hexane in raffinate. R: solvent to feed weight ratio).

**IV. PROPERTY PREDICTIONS**

ECOFAC uses correlations derived previously (Pretel et al., 1992) to estimate pure compound properties. The analysis of solvents and products from an environmental point of view also requires the knowledge or prediction of solution properties like solubility in water, Henry constants in aqueous solutions or partition coefficients in different systems. Especially the n-octanol/water partition coefficient of a solute have received a great industrial and legal interest in recent years. ECOFAC can perform these calculations using the LLE and VLE UNIFAC parameter tables, which has been discussed recently (Kuramochi et al., 1998; Derawi et al., 2001), and also using the “gamma infinite dilution” UNIFAC (Bastos et al., 1988).

Table 6: Predictions of the logarithm of the n-octanol-water partition coefficient (log K_{ow}) for some n-alkylbenzenes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sherblom et al. (1992)</th>
<th>UNIFAC LV</th>
<th>UNIFAC LL</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-decylbenzene</td>
<td>7.38</td>
<td>6.63</td>
<td>7.03</td>
</tr>
<tr>
<td>n-undecylbenzene</td>
<td>8.14</td>
<td>7.07</td>
<td>7.51</td>
</tr>
<tr>
<td>n-dodecylbenzene</td>
<td>8.65</td>
<td>7.50</td>
<td>7.98</td>
</tr>
<tr>
<td>n-tridecylbenzene</td>
<td>9.36</td>
<td>7.94</td>
<td>8.46</td>
</tr>
<tr>
<td>n-tetradecylbenzene</td>
<td>9.95</td>
<td>8.37</td>
<td>8.92</td>
</tr>
</tbody>
</table>

Predictions of the log K_{ow} with the LV and LL UNIFAC tables have been already reported in the literature for some n-alkanes, 1-alkanols, carboxylic acids, aldehydes and ketones (Derawi et al., 2001). In addition, we have tested the infinite dilution table, finding the highest deviations in this case for the families already mentioned. This is due to the high solubilities of most of these organic compounds in n-octanol, and in some cases also in water. In Table 6, ECOFAC predictions of log K_{ow} using the LV and LL tables are compared to the values reported by Sherblom et al. (1992) for Alkylbenzenes.

**V. CONCLUSIONS**

In the present work the ECOFAC approach for the solvent selection problem has been introduced. A procedure for the synthesis of branched molecular structures has been developed based on the use of metha groups and new characterization of the combination properties of the UNIFAC groups. A strategy for reducing the size of the combinatorial synthesis problem is presented. The evaluation of supercritical solvents based on rigorous simulation of the separation units is demonstrated by the optimization of the operation conditions for the de-terpenation of citrus oil and the removal of contaminants from natural oils. The possibilities of property prediction calculations using ECOFAC have been exemplified with the n-octanol-water partition coefficient.

**NOTATION**

J   Number of J groups.
K   Number of K groups.
NFA Number of free attachments in the intermediate structure.
NJF Number of J free attachments after combination of J groups only.

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**REFERENCES**


