BIODIESEL PROCESS DESIGN THROUGH A COMPUTER AIDED MOLECULAR DESIGN APPROACH

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Abstract
This paper proposes the application of computer-aided molecular design methods for the design of biodiesel processes. Solvents are used in two stages during bio diesel production. In the first stage solvents are used for extraction of oil from feedstock and in the second stage solvents are used to facilitate the conversion of oil into biodiesel. This paper introduces the application of state of the art computer-aided molecular design methodology for the design/selection of solvents for the conversion of oil seed feedstock to biodiesel. A case study involving design of co-solvents for the promotion of transesterification reaction during the production of biodiesel from soybean oil is presented. The designed co-solvent is intended to increase the reaction rate by forming a single phase solution of the reactants.

Keywords
Biodiesel, Co-solvent, Oil extraction, Transesterification, CAMD.

Introduction
Biodiesel production from feedstock such as soybean and algae involves two major steps a) extraction of oil from oil seeds and b) chemical conversion of extracted oil into biodiesel. The three common methods for extraction of oil from oil seeds are expeller/press method, solvent extraction method and supercritical fluid extraction method. There are other extraction methods such as enzymatic extraction and ultrasonic extraction that are less frequently used. Among these methods “solvent extraction” is the most frequently used approach. Solvent extraction method can be used in isolation or it can be combined with expeller/press method to extract oil. Typically hexane is used as a solvent in this approach. When combined with expeller/press method, first oil is extracted with the expeller and the residue pulp is mixed with the solvent whereby the remaining oil dissolves in the solvent. The residue pulp is filtered out and the oil is separated from the solvent by distillation. Once the oil has been extracted to the maximum extent possible, it is chemically converted to biodiesel through transesterification reaction. Chemical transesterification of oil involves reaction of a triglyceride (oil) with an alcohol (typically methanol) in the presence of a catalyst (typically a strong acid or base) to produce fatty acids alkyl esters (biodiesel) and glycerol. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants (Schuchardt et al., 1998). The presence of the catalyst accelerates the forward reaction. For an acid catalyzed process, the most commonly used catalysts are sulphuric acid and hydrochloric acid and this process is particularly effective if the vegetable oils have high free fatty acids content and more water (Yang and Xie, 2007). However the reaction
Role of Solvents in biodiesel production process

As discussed in the previous section solvents are used at various stages of the biodiesel production process. Particularly they are used for oil extraction and in certain cases they are used to facilitate the transesterification reaction. Till now promising solvents have been chosen based on bench scale experimentation and process knowledge. There has not been a systematic framework for design/selection of solvents for these processes. The solvents that are being used for oil extraction (e.g. cyclohexane) and esterification reaction (e.g. tetra hydro furan) have been selected on a trial and error basis. Moreover, when selecting a solvent it is imperative to consider environmental and safety issues (e.g. solvent toxicity, solvent flash point) in addition to the performance of solvents. In this paper we present a systematic computer-aided approach for solvent design/selection for biodiesel production.

Computer-aided solvent design

We propose an optimization based decomposition methodology (Karunanithi et al., 2005) for the design of chemical compounds (e.g. solvents) with specific properties from functional groups. The decomposition methodology involves an optimization approach in which the CAMD design problem is formulated as an optimization model where a performance requirement is posed as objective function and all other property requirements are posed as constraints. Group contribution models are used to evaluate the property constraints. Structural constraints are used to make sure that only feasible chemical compounds (solvents) are generated, i.e. compounds that satisfy valency criterion. Since both integer variables (structural) and continuous variables (e.g. mole fraction) are involved and since some of the property constraints are non-linear in nature we end up with a mixed integer non-linear programming (MINLP) optimization model. The solution to this optimization model provides the optimal molecular structure that satisfies all the property constraints with the minimal objective function value. A generic CAMD problem from Karunanithi et al. (2008) formulated as an MINLP optimization model is shown below:

\[
\begin{align*}
\text{Min} & \quad f_{\text{obj}}(X, Y), \\
\text{Subject to}, \\
\text{Structural constraints:} & \quad g_1(Y) \leq 0, \\
\text{Pure component property constraints:} & \quad g_2(Y) \leq 0, \\
\text{Mixture property constraints:} & \quad g_3(X, Y) \leq 0.
\end{align*}
\]

Process model constraints: \( g_4(X, Y) = 0 \).

Here, \( Y \) is a vector of binary variables (integer), which are related to the identities of the building blocks (functional groups). \( X \) is a vector of continuous variables, which are related to the mixture (e.g., compositions) and/or process variables (e.g., flow rates, temperatures etc.). \( f_{\text{obj}} \) is the performance objective function, defined in terms of molecule-process (performance) characteristics and/or cost that may be minimized or maximized. \( g_1 \) and \( g_2 \) are sets of structural constraints (related to feasibility of molecular structure) and pure component property constraints (related to properties-molecular structure relationships) respectively. \( g_3 \) and \( g_4 \) are mixture property (related to properties-mixture relationships) constraints and process model (related to process-molecule/mixture relationships) constraints respectively. The solution to this generic MINLP optimization model is achieved through a decomposition based solution methodology. Detailed description about the CAMD- MINLP optimization model and the decomposition based solution methodology can be found in Karunanithi et al. (2005). The decomposition methodology utilizes two programs ProCAMD (ICAS documentation. Internal report, 2003) and OPT-CAMD’ (Karunanithi et al., 2005)

Database search approach

Another approach to solvent selection is to use a solvent database to select solvents by matching property requirements. Examples of well known databases that can be used for this purpose are DIPPR and CAPEC database. The property requirements are posed as solvent search criteria and the database is searched to retrieve solvent candidates that match the criteria. The drawback in the database search approach is availability of all the compounds in the database and availability of property values. Also it is rare to find property values for mixture properties in a database.

Case Study: Solvent design for transesterification reaction

In this section a case study involving design of a co-solvent for the conversion of soybean oil into biodiesel through transesterification reaction is presented. As described in the first section the transesterification reaction involves the formation of vegetable oil methyl esters by the base catalysed reaction of triglycerides in the vegetable oil with methanol (Boocock, D.G.B., 2004). This reaction is known to be slow as it occurs in two phase. Low oil concentration in the methanol phase causes the slow reaction rate. The problem of the slow reaction rate can be overcome by using a co-solvent which results in the
transformation of the two-phase system to one-phase system (Boocock, D.G.B., 2004). The co-solvent should satisfy the following property requirements a) should be completely miscible with both methanol and the source of fatty acid triglyceride and should produce a homogenous single phase mixture of methanol-triglyceride-co solvent. b) co-solvent should have a boiling point of less than 393 K to facilitate solvent removal after the reaction is complete c) co-solvent should have a boiling point as close as possible to that of methanol in order to facilitate removal of both methanol and co-solvent in a single stage distillation unit. In addition the solvent should satisfy other process, safety and environmental constraints, namely d) should have high solubility for fatty acid triglyceride e) should be liquid at operating conditions f) should have high flash point and g) should have low toxicity. These property requirements are translated into property constraints that can be used in the CAMD model to design optimal co-solvent for this process. Toxicity is selected as the objective function that needs to be minimized. The proposed CAMD-MINLP optimization model for the design of co-solvent is shown below

\[
\text{Min} \left(-\log (LC_{50}) \right) \tag{1}
\]

Subject to

\[
\sum_i \sum_j u_{ij} (2 - \nu_j) = 2 \tag{2}
\]

\[
\sum_i \sum_j u_{ij} = N_{\text{max}} \tag{3}
\]

\[
\sum_j u_{ij} = 1 \tag{4}
\]

\[
17 < \delta < 19
\]

\[
\frac{1}{x_2} + \frac{\partial \ln \gamma_2}{\partial x_2} \geq 0 \tag{6}
\]

\[
325 < T_b = 204.359 \times \sum_i N_i T_{bi} + \sum_j M_j T_{bj} \geq 350 \tag{7}
\]

\[
T_m = 102.425 \times \sum_i N_i T_{mi} + \sum_j M_j T_{mj} \leq 270 \tag{8}
\]

\[
T_f = 3.63 \times \sum_i N_i T_{fi} + 0.409 \times T_b + 8843 > 200 \tag{9}
\]

\[
x_1 + x_2 + x_3 = 1 \tag{10}
\]

\(u_{ij}\) is a binary variable (special kind of integer variable) indicating whether the \(i^{th}\) position in a molecule has structural group \(j\). \(\nu_j\) represents valence of group \(j\). \(N_{\text{max}}\) represents maximum number of positions in a molecule. \(\delta\) represents the solubility parameter of the solvent. \(N_i\) is the number of times the first order group ‘\(i\)’ is present in the molecule. \(M_j\) is number of times the second order group ‘\(j\)’ is present in the molecule. \(T_f, T_m\) and \(T_m\) are the solvent flashpoint, boiling point and melting point respectively. \(T_{fi}, T_{bi}\) and \(T_{mj}\) are the contributions of first order groups towards flash point, melting point and boiling point respectively. \(T_{bj}\) and \(T_{mj}\) are the contributions of second order groups towards flash point, melting point and boiling point respectively. LC50, a measure of solvent toxicity, represents the aqueous concentration causing 50% mortality in fathead minnow after 96 hours. \(\gamma_i\) is the activity coefficient of component \(i\). \(H_{298}^{\text{Vap}}\) and \(V_{298}^m\) represents the heat of vaporization and molar volume of the solvent respectively. \(x_1, x_2\) and \(x_3\) are mole fraction of methanol, fatty acid triglyceride and solvent respectively. Equation (1) is the objective function where the toxicity of the solvent represented by \(-\log (LC_{50})\) needs to be minimized. Equation (2), (3) and (4) represent structural constraints that are used to make sure that only chemically feasible solvents are generated. Equation (5) is the constraint on solubility parameter to achieve high solubility of fatty acid triglyceride in the solvent. Equation (6) is the Gibbs phase rule constraint to achieve a homogeneous single phase mixture of methanol, triglyceride and co-solvent. Equation (7) is the constraint on boiling point to achieve easy removal of solvent and simultaneous separation of solvent and methanol after the completion of the reaction. Equation (8) is the constraint on melting point to maintain the solvent in the liquid state at operating conditions. Equation (9) is the safety constraint represented by flash point. The group contribution model proposed by Martin and Young (2001) is used for calculating \(-\log (LC_{50})\). The comprehensive data set from which this group contribution model was developed consisted of 397 organic compounds. This model was able to achieve a fairly good correlation of the data \((r^2=0.91)\). The solubility parameter, boiling point, melting point and flash point are calculated using Constantinou and Gani (1994) group contribution method. The reliability of Constantinou and Gani group contribution method is extremely high and compared to other group contribution models it demonstrates significant improvements in accuracy and applicability. The absolute percentage errors for boiling point and melting point calculated using Constantinou and Gani method are 1.42% and 7.23% (Constantinou and Gani, 1994). Solubility parameter is estimated through a correlation which utilizes heat of vaporization, which in turn is estimated using Constantinou and Gani method (absolute percentage error of 2.57%). Flash point is also estimated through a correlation that relates it to boiling
point. The activity coefficient is calculated using UNIFAC group contribution method (Fredenslund et al., 1975). Hence the reliability and accuracy of the utilized group contribution models are very high.

Results

The solution of the above optimization model using the decomposition methodology resulted in the optimal co-solvent structure shown in Fig. 2. The design results of the optimal solvent are shown in Table 1. Global optimality cannot be guaranteed with the decomposition methodology since the final MINLP sub-problem solved as a series of NLP problems uses a local optimization algorithm (OPT-CAMD'). However it is worth noting that the initial sub-problems solved using ProCAMD (ICAS documentation. Internal report, 2003) uses an enumeration approach and hence explores the search space effectively.

Figure 2: Optimal Co-Solvent- Methyl Ethyl Ketone

Table 1: Design Results- Property values of optimal co-solvent

<table>
<thead>
<tr>
<th>δ</th>
<th>T_i</th>
<th>T_m</th>
<th>T_b</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPa</td>
<td>K</td>
<td>K</td>
<td>K</td>
</tr>
<tr>
<td>18.76</td>
<td>262.42</td>
<td>187.97</td>
<td>343.82</td>
</tr>
</tbody>
</table>

Conclusions

This paper presents the application of a novel computer-aided tool for the design of biofuel processes. In particular it introduces the application of computer-aided molecular design approach for the design/seLECTION of solvents for biodiesel process. A generic CAMD methodology that can be used for this purpose is presented and the solution method for the model is described. A case study involving the design of a co-solvent to facilitate the conversion of soybean oil to biodiesel through transesterification reaction is shown. An optimal solvent is proposed for the discussed process.

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References


