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Renewable Raw Materials: chance and challenge for Computer-Aided Process Engineering

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Abstract

In the context of the climate change and with the perspective of rapid exhaustion of fossil hydrocarbon resources, the use of renewable raw materials becomes vital for the future of Chemical Process Industries. The first oil crisis from 1974 kicked-off the advent of process simulation. Today the emergence of bio-fuels, boosted by a serious petroleum and environmental crisis, is an exiting challenge for developing new design methods and simulation tools, as well as a chance for CAPE rejuvenation.

Keywords: Conceptual process design, biorefinery, sustainable processes

1. Introduction

The oil crisis in 1974 signed the birth of process simulators. The driving force was higher efficiency and better management of the plantwide material and heat balances, by improving the performance of intensive unit operations, namely distillation-based operations.

Today the humankind is faced with the treat of climate change combined with the perspective of the exhaustion of fossil hydrocarbon resources in few decades from now. There is a strong public pressure toward more sustainable manufacturing processes. The answer to this involves a massive use of renewable raw materials (RRM), which in turn needs new manufacturing

technologies. This challenge asks for a large innovation effort inside CAPE, by reinvigorating the design methods and computer simulation tools.

2. Biorefinery concept

2.1 Technology platforms

Following US National Renewable Energy Laboratory (NREL), biorefinery is a facility that integrates biomass conversion processes equipment to produce fuels, power, and value-added chemicals. The biorefinery concept is analogous with the today's petroleum refineries, which produce multiple fuels and products from petroleum. Fig. 1 presents the concept following researches conducted in different places in Europe, namely in The Netherlands [1-3].

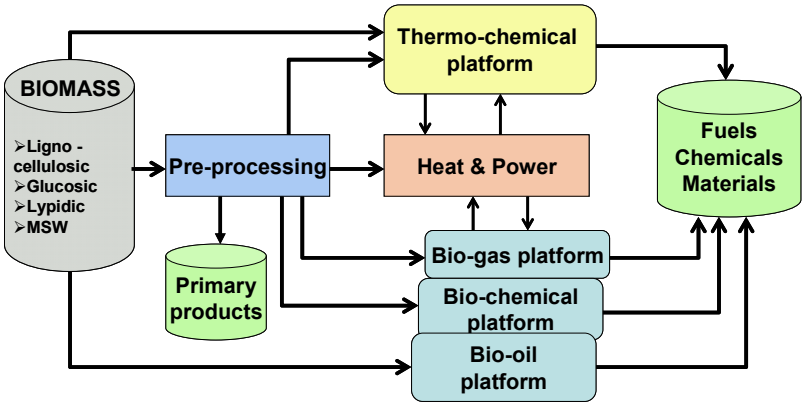

Figure 1 – The concept of biorefinery

The input of the plant consists of renewable or waste materials, as:

1- Lignocellulose (wood, straw, sugarcane bagasse, crop residues, etc.).
2- Cereals and maize grains.
3- Glucosic biomass: sugar-beet, sugarcane, potato starch.
4- Lipids: vegetable oils and animal fats.
5- Municipal Solid Waste (MSW).

In the first step, the biomass is submitted to *pre-processing* for direct extraction of primary products by adequate methods. An example is wood pyrolysis. Valuable chemicals are obtained, as alcohols, esters, phenols, as well as complex organic molecules, as guaiacol or syringol, which otherwise would require complicated organic synthesis routes. However, the separation of species in small concentration might be not economical. An alternative is the

conversion to oil by hydro-deoxygenation, and processing in conventional petroleum refineries.

The core process in biorefining consists of transforming the residual biomass into useful products, as fuels, chemicals, solvents and polymers. Several *technology platforms* have been identified, as follows:

1- Thermo-chemical refinery or biomass to liquid (BTL): conversion of syngas to fuels by Fisher-Tropsh synthesis.
2- Biochemical refinery: conversion of lignocellulosic and cellulosic biomass by fermentation to bio-ethanol.
3- Biogas platform: production of landfill natural gas from MSW.
4- Long-chain carbon refinery: conversion of oils and fats to biodiesel.
5- Plant products platform: chemicals by genetic engineering.

Note that the residues of biomass can serve to generate heat and power.

The most efficient use of RRM is by an *integrated-chain approach* of biorefinery & biochemical processes, analogue to a refinery & petrochemical complex. Beside high-volume low-value (HVLV) bio-fuels, low-volume high-value (LVHV) biochemicals are produced, with much higher economic profitability. For example, by assuming a yield of 10 t/ha biomass gives a net revenue of about 850 €/ha if fully converted in bio-fuels, but 6400 €/ha if producing chemicals [1].

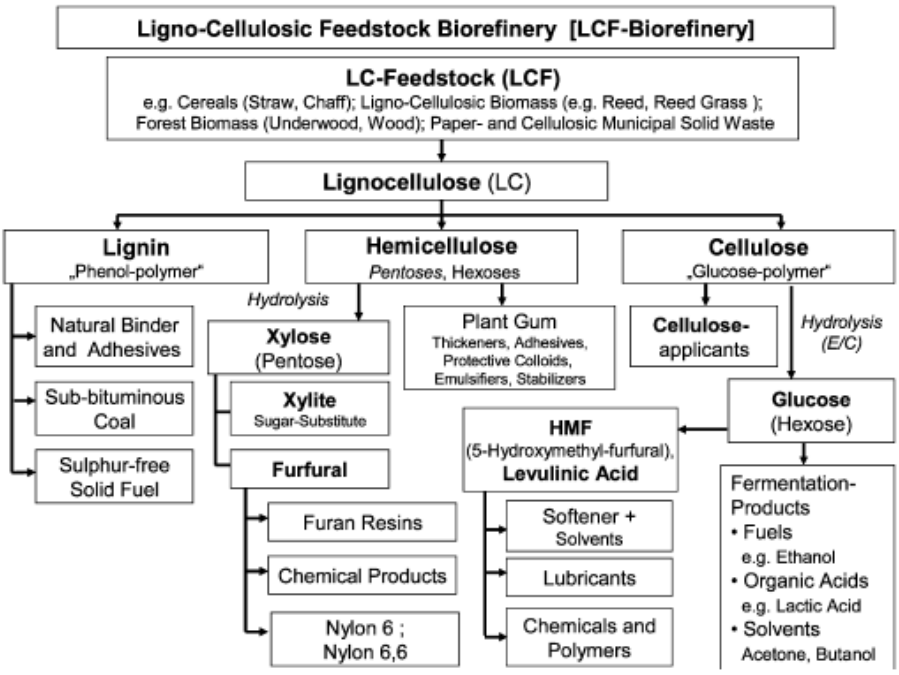

Fig. 2 - Ligno-cellulosic Feed-stock (LCF) biorefinery [2]

2.2 Building blocks

Building blocks are simple molecules on which further diversification in products is possible by organic synthesis. Thus, the catalogue of petrochemical products is built around C1, C2, C3, C4, C5 and BTX components. In opposition with petrochemistry, where larger hydrocarbons are chopped in small molecules by spending a large amount of energy, the biotechnology can offer the same building blocks with much better exergetic yield. Thus, the C1 chemistry can be organized around CH_4 got from bio-gas and methanol, C2 around ethanol and acetic acid, C3 around glycerol and lactic acid, etc., as shown in Fig. 3. Getting bulk BTX is more difficult, but natural complex aromatic molecules can be extracted with higher benefit.

Some examples: Traditionally acrylonitrile is obtained from C3= and NH_3. Alternative synthesis routes are possible from: 1) lactic acid, 2) acetaldehyde cyanohydrin, and 3) acetonitrile from syngas with NH_3 followed by oxidative methylation. New biodegradable polymers can be synthesized, as SORONA® from 1,3-propandiol, in turn obtained by enzymatic fermentation of maize. Specialty polyamides can be produced from castor oil, as Rilsan 11®.

Thermal coupling of reactions can greatly improve the energetic efficiency. Thus glycerol, a by-product by bio-diesel, can be converted to syngas using Pt catalyst. Conditions can be found for coupling this endothermic reaction (+350 kJ/mol) with the exothermic Fisher-Tropsh synthesis (-412 kcal/mol) [4].

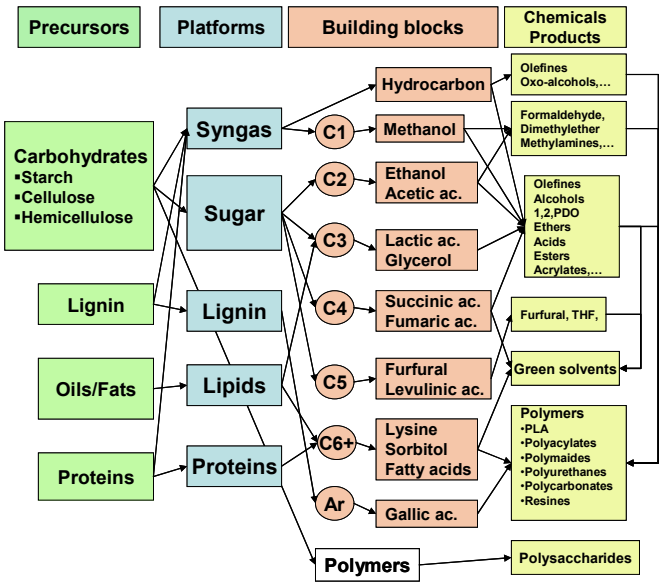

Fig. 3 – Building blocks for chemicals from renewable raw materials

3. The impact on design and simulation

3.1 Thermodynamic issues

The great virtue of molecular thermodynamics is in its broad range of applicability, which includes biotechnology and life sciences. Among the most important issues in biotechnology we can cite: 1) Prediction of properties of long-chain multi-functional bio-molecules; 2) Phase equilibria; 3) Structural and functional stability of proteins and bio-molecules, 4) Bio-catalysis: effects of pH, solvents, etc. 5) Driving forces and equilibrium.

The estimation of physical properties is challenging. The accuracy of today's methods, relying on group contributions extrapolated from small and simple molecules, is highly uncertain. The same is valid for mixtures. Because most of the biotechnological processes involve condensed-phase equilibria, the calculation of potentials and activities is much more demanding. Employing *molecular simulation* could offer a larger potential, but little experience amid CAPE community has been disseminated.

However, the network of relations among thermodynamic functions from classical thermodynamics can be exploited with surprising results. For example, the analogy between liquid activity coefficients, osmotic second virial coefficients (SVC) and solubility of macromolecules can help to solve design problems raised by conceptually different separation techniques, as chromatographic separations, precipitation and crystallization. In this way, the experimental information acquired for one system can be transferred to others. In addition, the analogy helps the selection of the appropriate experiments for getting data for model tuning. Moreover, bio-separations may be formally simulated by taking advantage from algorithms and models developed for petrochemical-like operations. Van de Wielen et al. presented a persuasive example for nystatin A [5]; the distribution coefficient needed for designing a chromatographic separation can be correlated by much simpler solubility measures with aqueous methanol solutions.

The following example, regarding the phase equilibrium of proteins due to Prausnitz [6], illustrates the power of thermodynamics in an even more complex domain, life sciences. Fig. 4 shows the metastable phase boundary of proteins contained in the eye. By aging, the content of proteins change, and one of more can "precipitate" when its concentration reaches saturation. This phenomenon can explain vision troubles or cataract formation. Curve a) shows the behaviour of a native liquid that segregates in two phases at 310 K (37 ºC), the phase with a concentration of 700 mg/cm^3 being responsible for disease. Adding a solvent (glutathione) helps avoiding protein segregation by forming a soluble complex.

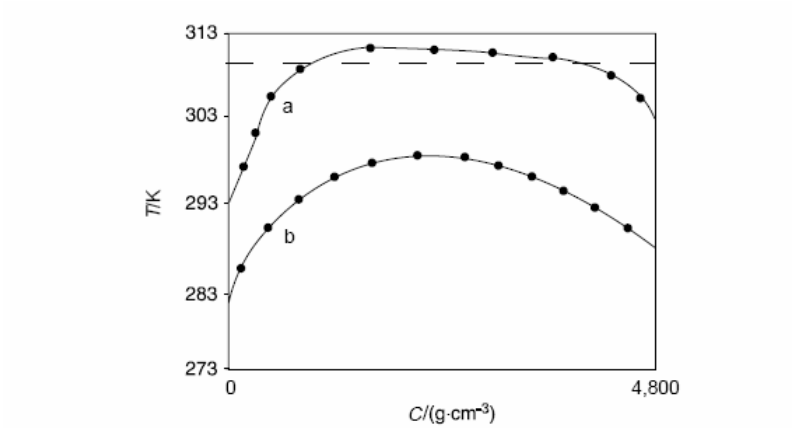

Fig. 4 Explanation of cataract formation by liquid-liquid segregation of proteins in the eye liquid [6]

3.2 Simulation issues

The modelling of processes involving RRM is demanding because of higher complexity of biochemical reactors, bio-separations and thermodynamics. The use of all-purpose simulators is not straightforward. On the other side, the development of dedicated software is constraint by a smaller market, but this situation could change with the boost in bio-fuels. An open system demands an important involvement of the user. The situation is complicated by the availability of few commercial systems. Therefore, before rushing to simulation a clear definition of goals, constraints and available tools is necessary.

In our view, the computer simulation may be useful in biorefinery and bio-chemical processes in the following applications:

1. Batch processes: receipt definition, process dynamics.
2. Flowsheeting and economic analysis.
3. Environmental protection.
4. Design of stand-alone units.
5. Study of stability and control of bio-chemical operations.
6. Scheduling and planning.

For continuous processes, as in biorefining, material balance by flowsheeting seems the most interesting. The reason is the necessity of handling the convergence of numerous recycles, when higher efficiency of RRM is aimed. In such case, mastering the interactions due to flexibility in feedstock is dominant over the detailed design of units.

Accurate calculation of physical properties and phase equilibria is the biggest challenge. Therefore, comprehensive simulators should be provided

with advanced thermodynamic capabilities, in particular for aqueous solutions and electrolytes, as well as with versatile algorithms for solving equilibrium based separation problems.

Existing commercial systems provided with user modelling capabilities, as Aspen Custom Modeller™ and g-Proms™, can be adapted for analysis and design, with the advantage of powerful mathematical methods. Super ProDesigner® (www.intelligen.com) is a dedicated package. It is provided with functional units and operational procedures specific for batch processes, but it can handle flowsheeting of continuous processes too. Solver-oriented packages can be helpful for off-line design and control studies, as Matlab™ and Stella™.

4. Application examples

4.1 Biodiesel process

Figure 5 depicts a conceptual scheme for biodiesel manufacturing from vegetable oils. In the first unit, reactor *R-1*, the esterification of free fatty acids (FFA) with methanol is carried out, preferably by reactive distillation. Resin ion-exchange catalyst can be employed at temperatures bellow 100 °C, or super-acidic sulphated zirconia at higher temperatures [7]. The amount of FFA should be reduced bellow 1%, as requested by transesterification, which takes place in the reactor *R-2*. Homogeneous basic catalysts are commonly used. The reaction mixture separates in crude ester and glycerol. The first product follows the finishing route: methanol separation, catalyst neutralisation, washing and drying. The 50% glycerol solution is treated with acid for recovering FFA, and then it is submitted to methanol recovery by simple flash. Glycerol of 85% is obtained as valuable by-product.

The simulation of a flowsheet close to the above scheme was done with Aspen Plus™ and SuperPro Designer® [8]. The economic analysis showed that 1/3 from the equipment cost represents storage facilities, while the feedstock counts for 88% from the production costs. Hence, smaller units can be efficient and easy to operate for biodiesel, in contrast with crude oil refining. The sensitivity to raw materials suggests that dedicated and mobile processing units could be suitable, adapted for processing local available raw materials. In order to succeed this, using a solid basic catalyst for transesterification instead homogeneous catalyst is necessary. This would simplify tremendously the design and make the plant more compact, by generalising the application of the reactive distillation to the whole flowsheet.

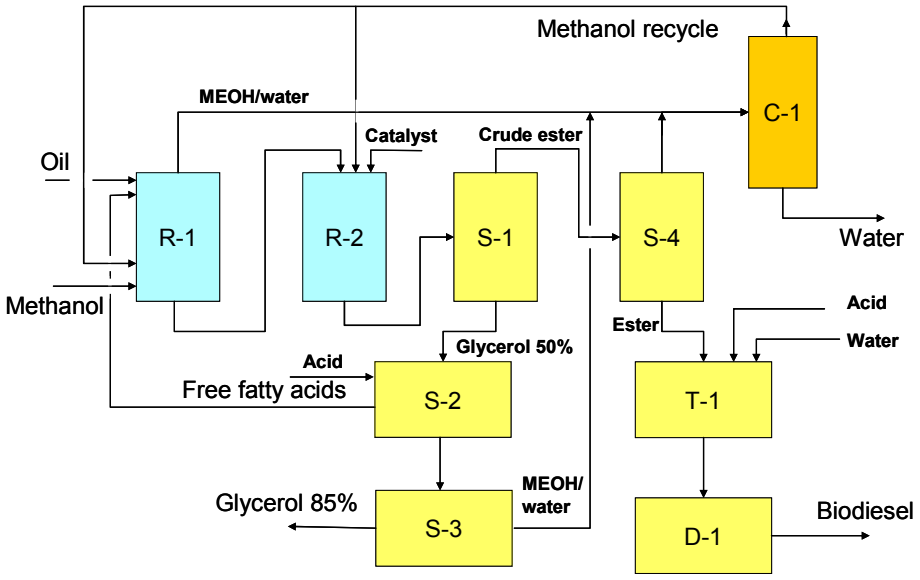

Fig.5 Flowsheet for biodiesel production

4.2 ω-Aminoundecanoic acid from castor oil

Rilsan 11® is a high-performance polymer, namely with applications in the automotive industry. Today is manufactured exclusively by Arkema in France (www.arkema.fr). The monomer, ω-aminoundecanoic acid, is obtained from a renewable material, the castor oil, a triglyceride of the ricinoleic acid (C18).

Fig. 6 presents a simplified scheme. Firstly, the triglyceride is transesterified in the reactor *R-1* to C18-methyl ester by using a large excess of methanol and homogenous basic catalysis. Neutralization and washing takes place in several stages, here symbolized by the black-box unit *S-1*. The organic phase goes to ester purification in *C-1*, while the aqueous phase to glycerol recovery in *S-2*. Next, the ester is submitted to pyrolysis in *R-2* at about 300 °C. It is interesting to note that the ricinoleic acid has a special structure among fatty acids, namely the presence of -OH next to C=C bound. Consequently, the molecule splits preferentially into heptanal (C7) and the C11-methylic ester of undecenoic acid (C1=). Heptanal is a valuable by-product with applications in perfumery. Further separation takes place in (C-3). Then the (C11=)methyl ester is saponified to (C11=)acid, which in turn is converted with HBr into 11-bromoundecanoic acid (anti-Markovnikov addition in the presence of peroxide). Finally, the reaction with NH_3 leads to the formation of an ammonium salt, from which the final product, the ω-aminoundecanoic acid, is obtained.

The plant flowsheet is actually much more complicated. However, it can be analysed based on three large recycles: methanol, fatty ester and water. The last is the trickiest, since the process implies complicated neutralization, washing and decantation stages. The control of these operations by pH and phase split is essential. In addition, keeping an acceptable impurity level in the recycled water is necessary. Controlled purity of water is obtained by evaporation, and as result material and heat balance are interdependent. The coupling can be pushed to the limit of complete process water recycling. For such application, building a complex Plant Simulation Model is profitable both for managing the daily plant operation and for design purposes [9].

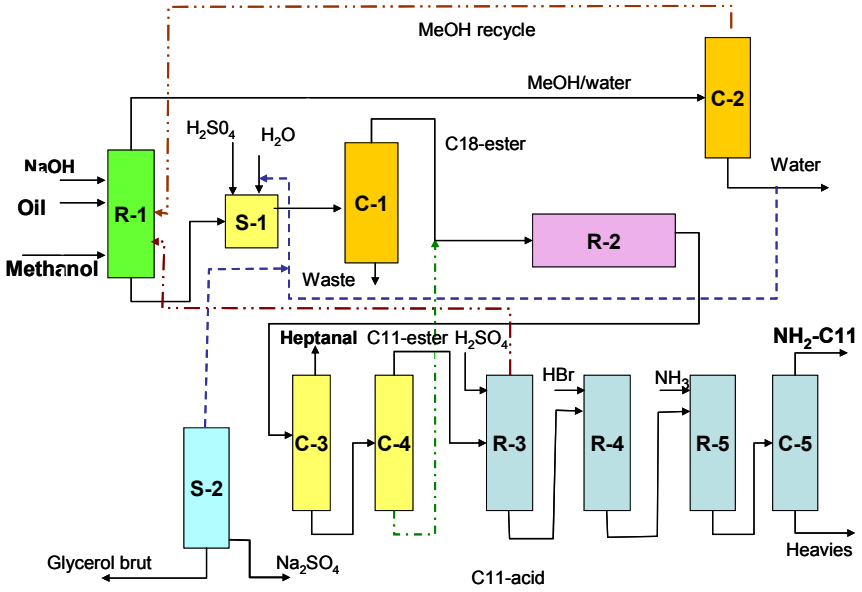

Fig. 5 Flowsheet for the synthesis of ω-aminoundecanoic acid from castor oil

5. Conclusions

The use of renewable raw materials opens large opportunities for CAPE, but raises also a number of issues regarding the process design approach. Difficulties originate from the larger variability of renewable raw materials and from complex chemistry, physical properties and phase equilibria, as well as due to specific techniques for biochemical reactions and separations. Because of vital economic importance, the manufacture of bio-fuels can be the cradle of new design concepts and a boost for simulation tools.

The biorefinery concept enables the structuring of the technology needed to ensure efficient biomass conversion to fuels and power. Much higher efficiency

results out by integrating biorefinery with biochemical and organic synthesis processes, since bio- building block molecules need low energy consumption. The precursors C2 and C3, as well as the syngas are particular versatile. In this way, renewable raw materials could supply a large part of the petrochemical intermediates, as well as solvents and polymers.

The simulation of biotechnological processes with the existing all-purpose packages is not straightforward. However, these can be adapted for handling some design aspects, namely material and heat balance problems. A major challenge is the computation of physical properties and equilibria. The imbedding of specific models needs an open modelling environment.

Two examples, biodiesel and polyamide, show that CAPE tools can be used for solving challenging design and operation problems raised by the more complex nature of raw materials. Significant progress can be achieved by using solid catalysts to influence the chemistry in terms of selectivity and productivity. The flowsheet of a biorefinery could reach a high degree of compactness by using process intensification design, namely reactive distillation. Small-scale or even mobile units specialised on feedstock can be cost-efficient, in contrast with the giant oil refinery plants.

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