# The Role of Digital Technology in Biofeedstocks, Value Chemicals and Fuels

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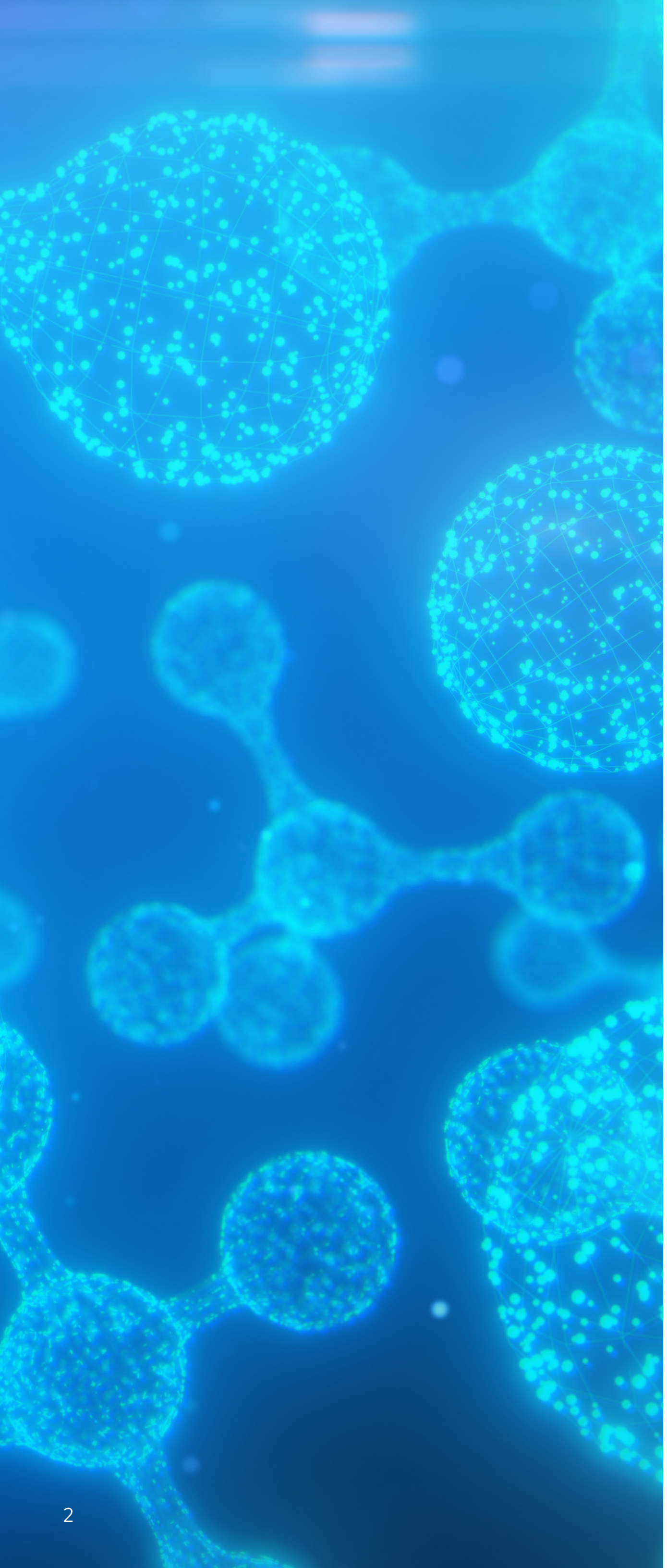
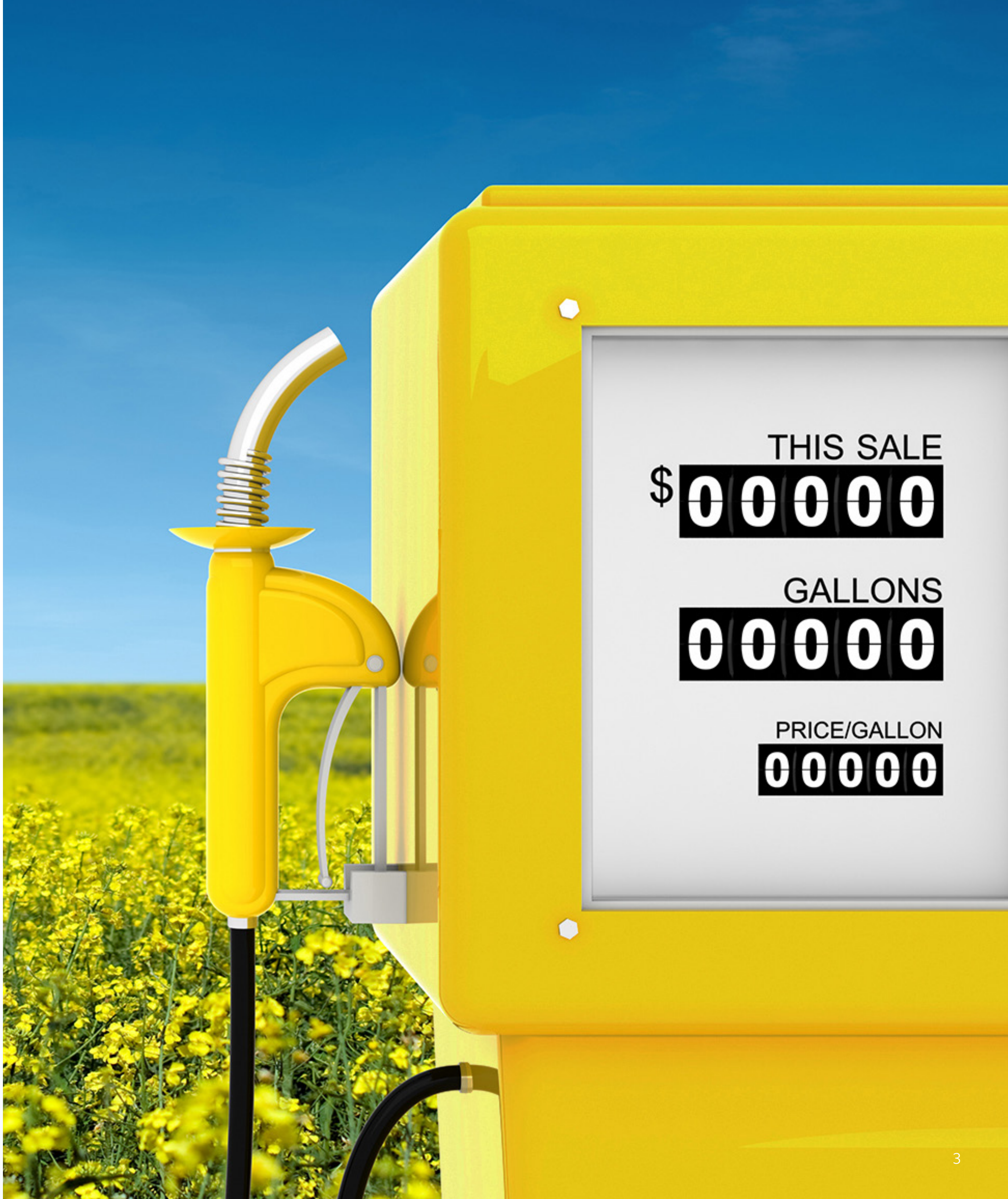


# Introduction

With growing economies, the world is facing the dual challenge of addressing the critical resource needs of an expanding population while reducing the environmental and ecological impacts of using fossil-based energy sources. Bio-based energy and chemicals resources can play a prominent role in tackling this challenge. Bio-based feedstocks are an important piece of creating a circular economy where non-renewable resources are replaced using renewable resources. Renewable feedstocks can transform rural economies and the process to make them is generally safe with less adverse end-of-life effect for the environment. Additionally, biofeedstock production and use has a lower carbon footprint than the existing fossil fuels. Despite these advantages, many chemical and polymer makers have been reluctant to actively pursue large-scale use of bio-based feedstocks, largely because of the availability of cheap fossil fuels over the past decade.

Historically, bioethanol has captured over 80% of the biochemicals market with its main use as biofuel.[1] Production of other bulk chemicals through biomass processing remains non-competitive. Shifting geopolitical conditions and cyclic high fossil fuel prices present an opportunity in the investment and development of sustainable chemicals. In recent years, biorefineries are increasingly being seen as an economically viable method for producing bio-based fuels and chemicals.[1] Using first generation biomass (e.g., corn, soy and sugar cane) remains unfavorable by the public or policy makers to produce fuels and chemicals. However, the new generation of bio-based chemicals and fuels use lignocellulosic biomass along with inedible oil seed crops as feedstock in integrated biorefineries.[2] As part of the Inflation Reduction Act of 2022 to boost clean energy and fuels transition in the US, second generation biofuels producers can receive a credit of up to $1.01/gal. Qualified feedstocks include any lignocellulosic or hemicellulosic matter that is available on a renewable or recurring basis as well as any cultivated algae, cyanobacteria or lemna.[3]

Apart from fibers like cellulose, hemicellulose and lignin, carbohydrates like starches, sugars, oils, fats and proteins are typical bio-based feedstock components.[2] Many of these components, like used cooking oil can be recovered from waste streams. However, working with waste stream brings up practical challenges. For example, the composition of a particular stream can vary significantly, depending on the source. Therefore, biomass transformation processes can become complex quickly and choosing proper applications based on biomass properties is crucial. Additionally, with a complex feed stream, there is a need for a complex processing plant. Biofeedstock processing facilities are generally referred to as "biorefinery" to capture variability in composition and processing needs, similar to fossil based crude oil.



There is an abundance of processing intricacies for biofeedstocks. Lignocellulose, for example, can go through a gasification process to make syngas which can be subsequently transformed to methanol, olefins and BTX. Alternatively, with pretreatment, it can be transformed to cellulose and hemicellulose to make C5 and C6 sugars. Transformation of sugars is another important pathway in creating valuable chemicals from biofeedstocks. Through fermentation, these sugars can be transformed into hydrocarbons (e.g., isoprene, butadiene, etc.), acids (e.g., adipic acid, lactic acid or acrylic acid), or into alcohols and di-alcohols (e.g., ethanol, 1,3-propane diol, etc.). The catalytic treatment of these sugars can create kerosene, aromatics (BTX) or gasoline components. Similarly, inedible plant oils, waste oils and fats are sources of triglycerides. Upon alcohol treatment, triglycerides can transform into glycerol, fatty acids and alcohol esters. Through catalytic dehydration, glycerol can turn into high value chemicals like acrolein and subsequently acrylic acid. Through fermentation, fatty acids can make dicarboxylic acids or turn into epoxides through chemoenzymatic treatments.

In general, after feedstock pretreatment (which varies depending on feedstock type and technique such as physical, chemical, biological, mechanical, or a combination of them), pyrolysis or fermentation are used to process the treated feedstock. Pyrolysis is a cost-effective and scalable process to turn biomass into energy and valuable chemicals. However, adjusting pyrolysis parameters plays a key role in the quantity and quality of materials produced. Similarly, many valuable chemicals such as organic acids, alcohol and ketones, industrial enzymes and bio-polymers (bio-PBT, PP, PHA, PLA, etc.) are products of fermentation. Designing a fermentation process can similarly be complicated as much of the research is conducted via small set-ups and scaling up to optimal yields remains difficult. Digital solutions are game changers to address these design and scale up challenges and to deliver desired products with the least time and upfront capital investments.

# The Critical Role of Digital Technologies

As the complexity of biofeedstocks has increased, the need for digital solutions to build better processes has become more pressing. Creating and scaling new processes requires a significant amount of experimental work to check feasibility, economics, yield and viability of a new process. Digital technologies can help to cut back on the number of required experiments or help to design a more targeted experimental scheme. When it comes to scale up, digitalization can be used to evaluate economics and offer design solutions to improve process efficiency. AI-enabled solutions can improve model predictions, especially when there is a gap in the experimental data or there is variability in product quality.

Over the years, numerous studies have been performed to make biofuel or bio-based chemicals leveraging digital solutions. The results of perhaps one of the most complete studies performed to date were published in an April 2022 report by the National Renewable Energy Laboratory on conversion of lignocellulosic biomass to hydrocarbon fuels and products using Aspen Plus® models.[4] With market demand for processing biofeedstock growing, digital solutions can offer more sophisticated tools to accurately model these processes.

In the following sections, we look at examples of biofeedstock processing using the AspenTech® Performance Engineering suite.

## Characterization of Renewable Feedstocks

Due to the diversity of biofeedstocks, appropriate characterization of components is essential to properly simulate and optimize the process. As previously discussed, plant-based feedstocks or animal fats can be characterized as bio-based feedstocks. Let's review how biofeed and biodiesel databanks within Aspen Plus as well as vegetable oil templates within Aspen HYSYS® cover a wide range of lignocellulosic biomass and vegetable oil-based feedstocks.

### Biofeed Databank

Within Aspen Plus, the biofeed databank lists more than 500 different feedstocks from agricultural/industrial/municipal waste to micro/macroalgae, grasses, hardwood and softwood sources. These feedstocks are listed along with their atomic composition, heat of formation and density information. Some examples include: C5 and C6 carbohydrate monomer components (cellulose monomer, hardwood hemicellulose, acetylated C5 hemicellulose, acetylated C6 hemicellulose, etc.). Basic lignin monomers along with intracellular water, extractives and structural biomolecules that do not classify as carbohydrates or lignin are other examples of the listed components. One example of agricultural waste (major components of almond shell) is listed below (Table 1).

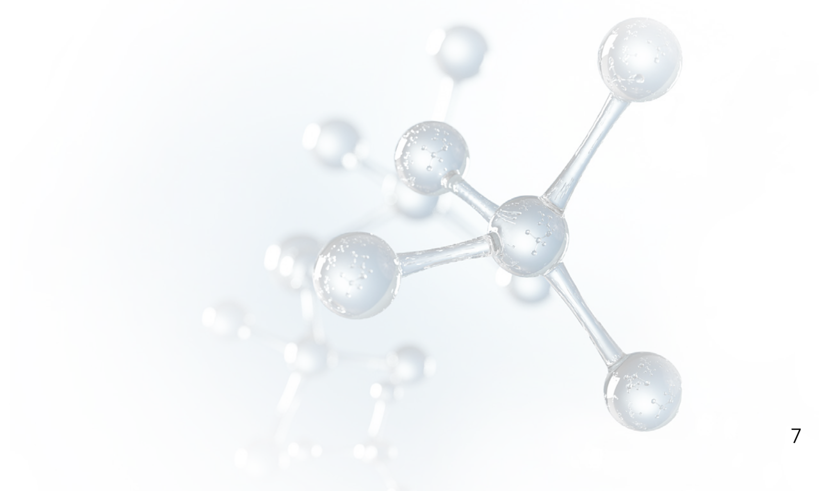
| Component | Mass Fraction |
|---|---|
| BIOMASS-CELLULOSE | 0.390219 |
| BIOMASS-XYLAN | 0.260146 |
| C-RICH-LIGNIN | 0.017928 |
| H-RICH-LIGNIN | 0.000014 |
| O-RICH-LIGNIN | 0.117279 |
| WATER-SOLUBLE-EXTRACTIVES | 0.214414 |

Table 1. Characterization example: agricultural waste, almond shell

The feedstock compositions in biofeeds are specified on a dry, ash-free (DAF) basis, enabling users to customize the level of moisture as well as the amount and type of ash content in the feedstock (commonly silicon, calcium, phosphorus and potassium). Any component not listed in the biofeed databank can be defined as a non-conventional component. In this way, thousands of components from whole plants, plant fractions, pretreated biomass, micro- and macroalgae can be defined and added to the databank. This databank lowers the modeling expertise barrier for average process engineers to model lignocellulosic biomass feedstock characterization and corresponding conversion processes.

## Biodiesel Databank

Biodiesel is a renewable alternative diesel fuel consisting of short chain alkyl esters, made by transesterification of vegetable oils such as those from corn, olive, palm and sunflower or animal fats such as tallow, lardand butter, as well as commercial products such as margarines. Triglyceride is the main constituent of vegetable oils and animal fats. Multiple components contribute to the physical properties of a given oil, fat or triglyceride mixture. The triglycerides composition vary depending on the source of the oil and environmental conditions. One methodology to estimate the physical properties of an oil or fat can be using the average properties of involved fragments.



The biodiesel databank in Aspen Properties® contains over 400 triglycerides formed with eight common fatty acid fragments, with molecular weight, normal boiling point, critical temperature, critical pressure, vapor pressure, heat of vaporization, liquid heat capacity, heat of formation, liquid density and liquid viscosity based on constituting fragments. The thermodynamics and transport properties model parameters have been regressed from the literature data. The predictive model can then estimate the properties of pure or triglyceride mixture corresponding to the known fatty acid or triglyceride composition.

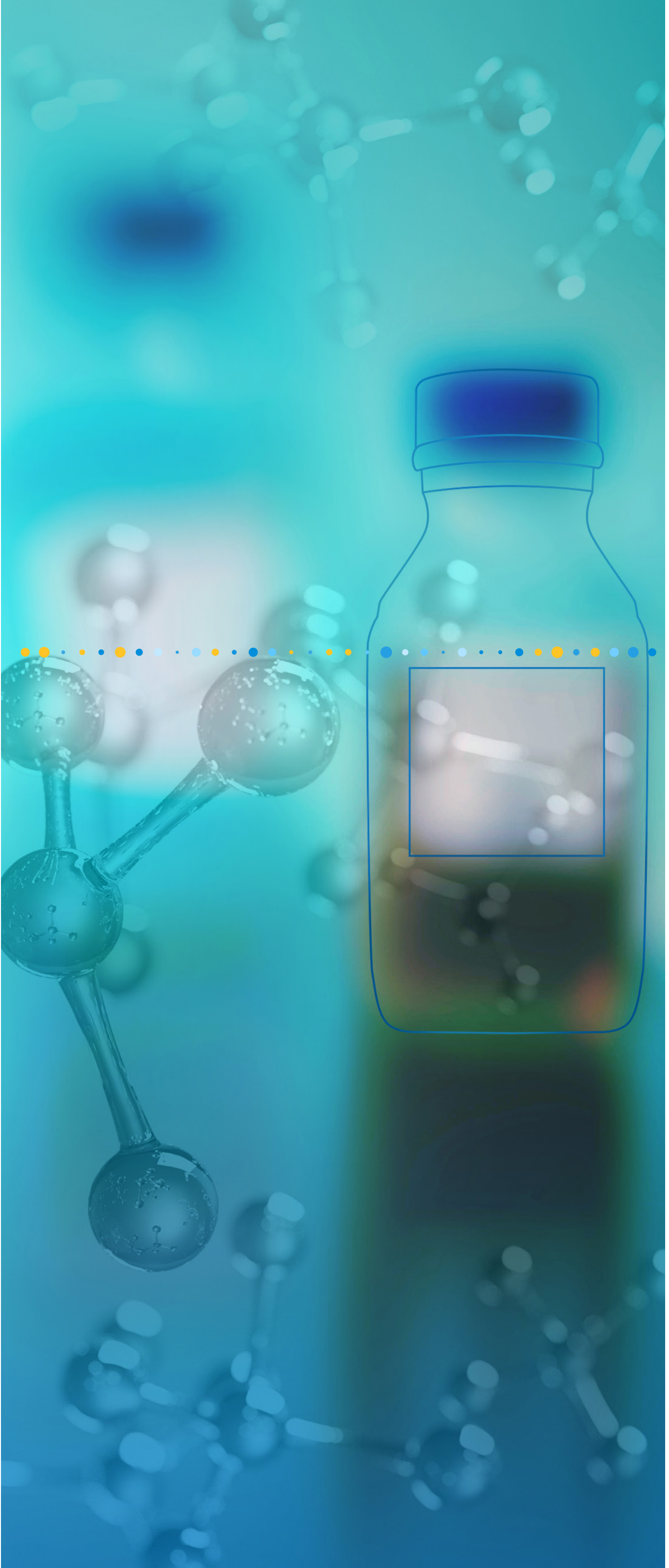
## Biofeed, Biodiesel Databanks Success Story: Novozymes

Novozymes, the world's largest provider of enzymes and microbial technologies, leverages Aspen Plus biofeed and biodiesel databanks to simulate and scale-up biodiesel processes. Combining the capabilities of Aspen Plus and the biodiesel production expertise of the Novozymes team, the company has successfully validated business cases, performed feasibility studies and accurately identified opportunities to maximize yield and profits in all stages of process development. Novozymes has lowered design costs and accelerated time-to-market by implementing these technologies.

novozymes®

### Vegetable Oil Templates

In addition to biodiesel production via transesterification, another approach for diesel production is hydro-processing of triglycerides into straight-chain paraffins. The latter is often referred to as green diesel production. Aspen HYSYS has a new template to characterize green diesel production using a molecular-based framework. The available feed types are avocado oil, castor oil, coconut oil, corn oil, cottonseed oil, olive oil, palm oil, rapeseed oil, soybean oil, tallow animal fats and waste cooking oil. In addition to the incoming feed type, two reactor models are predefined in Aspen HYSYS to assist biofeed processing designs. The first is a HDO Bed (hydrodeoxygenation) reactor,



which enables conversion of biofeed to hydrocarbons. The second reactor model is for co-feed (i.e., a mixture of biofeed and hydrocarbon feed) hydroprocessing and operates as a combination of a HDO Bed and hydroprocessing bed.

## Molecular-Based Modeling Success Story: HPCL

Indian refining company HPCL used molecular modeling technology to simulate hydrotreatment of used cooking oil. The model leveraged both experimental and literature data, along with Aspen HYSYS capabilities to obtain an optimal representation of the waste cooking oil feed. Aspen HYSYS' molecular-based reactor generated over 200 reactions and over 90 species to represent the decarboxylation, decarbonization and hydrodeoxygenation reaction paths.

## Modeling Bioprocesses

Processes that convert lignocellulosic or oil-based biomass to fuels and chemicals are broadly classified as biochemical or thermochemical processes. In biochemical (fermentation) processes, the first step is hydrolyzing biomass carbohydrate fraction (cellulose and hemicellulose) into sugar monomers that can be fermented. The lignin fraction is then converted separately or burned for energy. In thermochemical conversion processes that yield a complex bio-oil (pyrolysis) or syngas (gasification), the entire biomass is processed in one step without deconstruction.

### Fermentation

The Aspen Plus ferment database includes a wide variety of predefined cell types and common organisms, including bacteria, yeast, fungi and mammalian cells with elemental composition and corresponding properties. Ultimate analysis (i.e., CHNO analysis) is used to estimate enthalpy, density and heat capacity of biological components.

To model fermentation reactions, Aspen Plus offers a built-in library of customizable kinetic models. Mass yields are used to calculate overall mass balance in the bioreactor. The lifecycle of biological organisms (activation, growth, death) and batch, semi-batch or CSTR modes of operation enable users to simulate realistic fermentation conditions. As a result, systems with complex kinetics (rigorous pH calculations, multiple substrates, and products, anaerobic or aerobic processes) are closely modeled. These models can be calibrated to experimental/plant data using conventional parameter estimation techniques or a hybrid modeling approach that leverages AI to close the gap between model predictions and existing data (steady-state models only).

***Production of 600 kg of 1,4-butanediol (BDO) in a batch process using Aspen Plus***

1,4-butanediol (BDO) is an important industrial chemical with applications as a solvent or a precursor to other important chemicals like tetrahydrofuran and γ-butyrolactone. BDO is typically industrially produced by catalyzed oxidation of butane. However, microbe-assisted biological routes provide an alternative sustainable pathway for BDO production. Glucose or other renewable plant-based sugar mixtures can be used as the sustainable feedstock for fermentation while metabolically engineered organisms catalyze the reaction.

Figure 1 displays a snapshot of the semi-batch production model of BDO built in Aspen Plus. The continuous charge streams to the reactor include biomass, substrate, KOH for pH control and nitrogen. A sparging air stream is used to carry fermentation reactions in aerobic conditions. The produced gases are vented. In the product stream, BDO and some liquid impurities (acetate, ethanol, gamma-hydroxybutyric acid, gamma-butyrolactone, and an extracellular protein component) are obtained.

A generic microbe (dry cell mass or BioDCM) is defined as the enzyme to catalyze the reaction. Biomass growth rate is limited by the oxygen

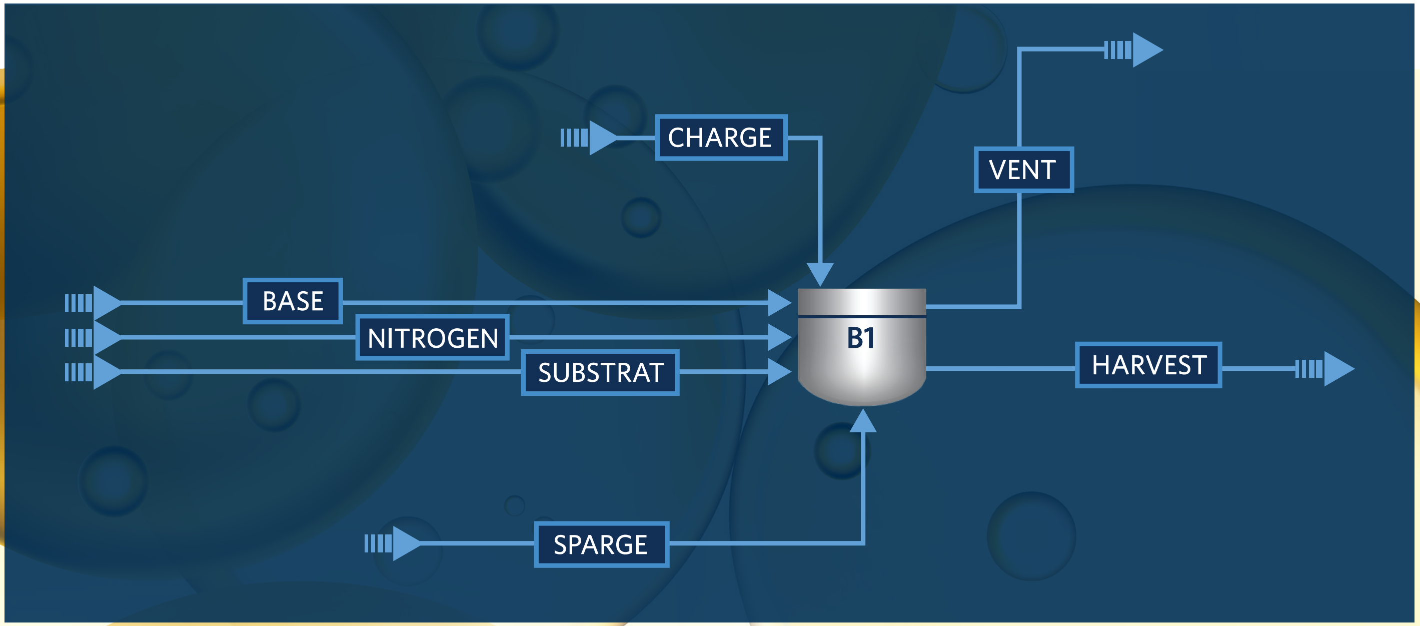



Figure 1. Semi-batch bioreactor inputs and outputs to produce 1,4-butanediol.

mass transfer rate. Therefore, the reaction includes an oxygen limitation term for this aerobic case. The atomic analysis (CHON) on mass or molar basis and the wt% ash (inert) can be specified for BioDCM and the protein obtained in the product stream. Formation of impurities is also considered in kinetics where it is assumed that the reactor is held at a constant temperature.

Figure 2 illustrates the production rate of BDO along with glucose, oxygen and carbon dioxide concentrations. Other impurities concentrations can also be plotted if needed. After the fermentation step, the resulting broth is furthered processed to separate BDO from all other components. Through building this model, estimated reaction time, yield and downstream required processing investments can be evaluated. This information enables decision makers to assess the feasibility of the design and its potential productivity.

## Pyrolysis

Biomass conversion processes based on pyrolysis offer high potential yields of liquid transportation fuels such as gasoline and diesel blend stocks, or refinery-compatible intermediates. In principle, the carbon efficiency of pyrolysis conversion is higher than that of fermentation or other sugar-based processes where biomass must be fractionated into carbohydrates and lignin before conversion. Fast pyrolysis of biomass proceeds by heating dried and prepared biomass to an intermediate temperature where volatilization begins but gasification (i.e., conversion to syngas) to vapor-phase products is not complete. Fast pyrolysis thus generates a liquid bio-oil that has roughly the same energy density as the starting biomass, but which can be transported more efficiently and potentially upgraded to fuels.

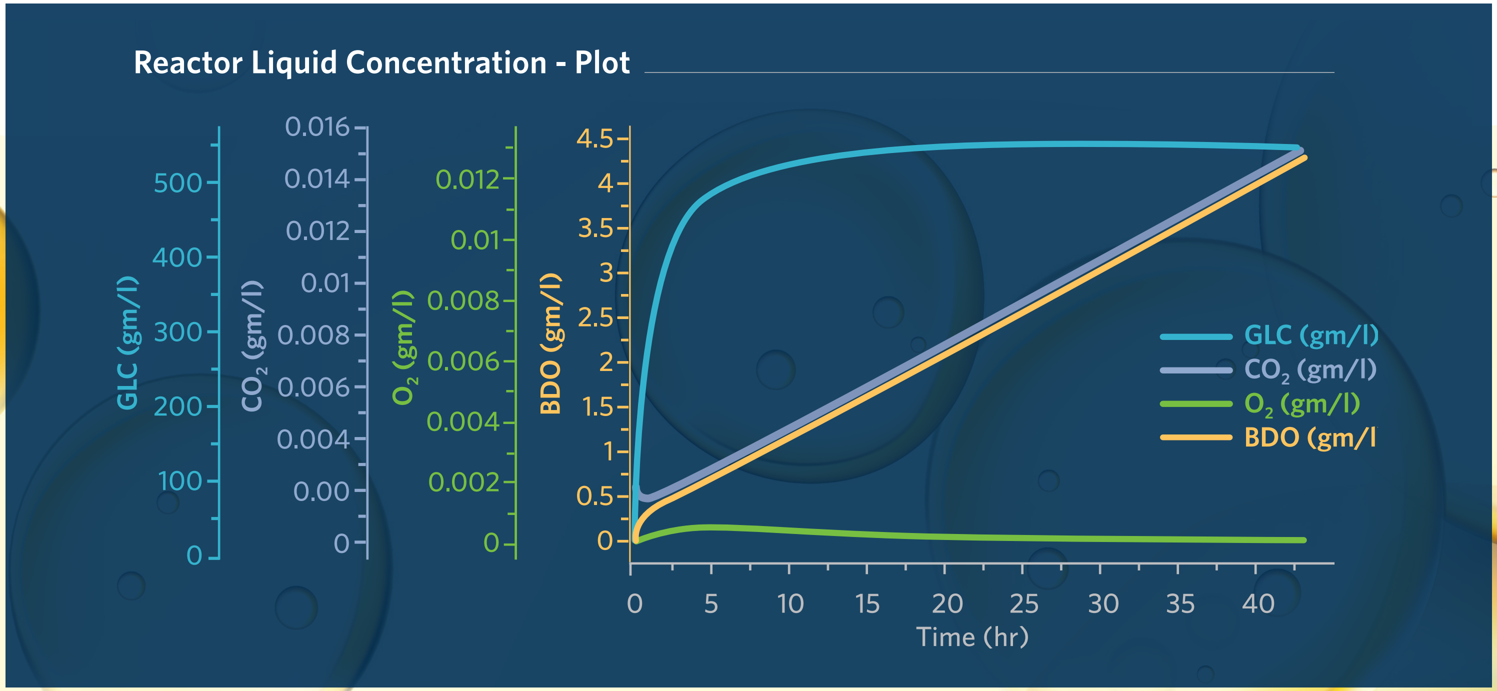



Figure 2. Aspen Plus generated composition plot shows the liquid phase concentration changes within the reactor through the reaction time. GLC here refers to the concentration of glucose as it builds up in the reactor.

To address the simulating complexities of a pyrolysis process, the following conditions must be met:

1. The databank should be able to account for intermediate and product components that are real molecules but are not found in the pure components library.

2. Oligosaccharides that are soluble but (usually) not fermentable species should be modeled as fully hydrolyzed sugars with the formula and DHFORM of the polymer unit.

With Aspen Plus, the NIST-TRC databank offers starting points for many such molecules, though the user may have to specify DHFORM and some auxiliary properties. Other intermediates and products such as small organic acids, aldehydes, and furfural can be found in the Aspen Properties enterprise database pure components along with mono- and disaccharide sugars. Uronic acids and other rarely used molecules are typically user defined.

*Fast Pyrolysis of Dry Soft Wood*

The yield and feasibility of fuel production reactions can be estimated using Aspen Plus models and databases. As an example, here we review conversion of 1,000 MT/d of dry wood feedstock to bio-oil. Dry soft wood is listed in the biofeed library as DOUGLAS-FIR-2 (Alias SWOOD-014).

| ID in Simulation | Component Name | Alias | DAF wt% |
|---|---|---|---|
| CELL | BIOMASS-CELLULOSE | C6H10O5-B1 | 44.06% |
| GMSW | BIOMASS-GLUCOMANNAN | C5H8O4-B1 | 22.01% |
| LIGC | C-RICH-LIGNIN | C15H14O4-B1 | 4.73% |
| LIGH | H-RICH-LIGNIN | C22H28O9-B1 | 12.05% |
| LIGO | O-RICH-LIGNIN | C20H22O10-B1 | 10.89% |
| TGL | WATER-INSOLUBLE-EXTRACTIVES | C57H100O7-B1 | 5.01% |

Table 2. Dry softwood feedstock composition

Note: Only the main components defined in biofeed are listed above.

The core conversion is modeled with a one-dimensional reactor that leverages fast pyrolysis kinetics. This reactor model captures the char combustor, quench loop, and gas and sand recycle loops in an Aspen Plus flowsheet. The reactor captures fluidization through interphase momentum transfer, interphase heat transfer via the gas phase (sand to gas and gas to biomass) and pyrolysis reactions in the biomass phase. Figure 3 displays a simplified flow diagram of the design.

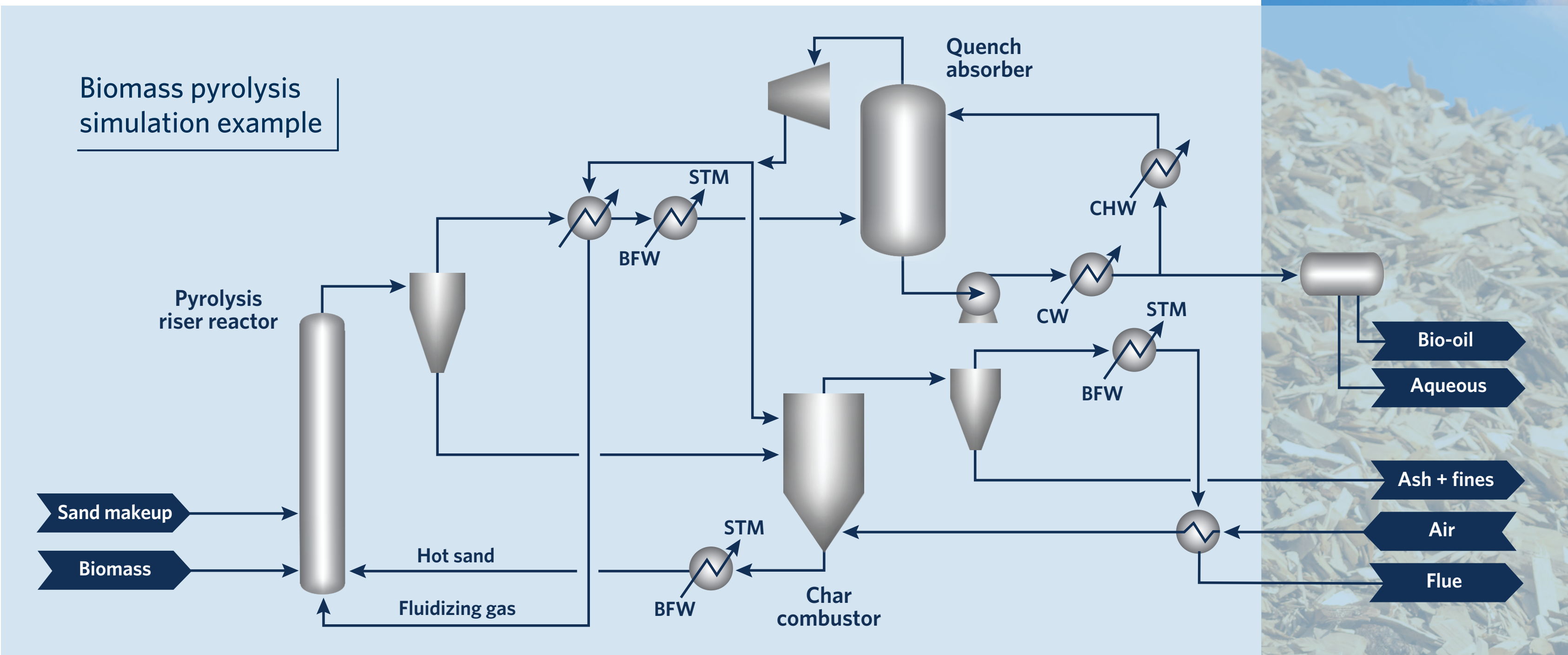



Figure 3. Biomass pyrolysis simulation example.

Based on this simulation, the products shown at right will be generated.

The flowsheet illustrates a model for the integration of pyrolysis kinetics and fluidization physics. The biocomponent definitions and process configurations can be modified to match existing experimental results. Process integration and data fitting features enable users to model and optimize conversion of lignocellulosic biomass (like dry woods here) to pyrolysis oil in large scale. The pyrolysis oil products can then be transported and processed further to produce renewable fuels in downstream processing.

**Carbon Flow**

| | | |
|---|---|---|
| Incoming biomass | 20,629 kg/h | |
| Bio-oil | 8,894 kg/h | 43% |
| Aqueous loss | 241 kg/h | 1% |
| Flue gas loss | 11,494 kg/h | 56% |

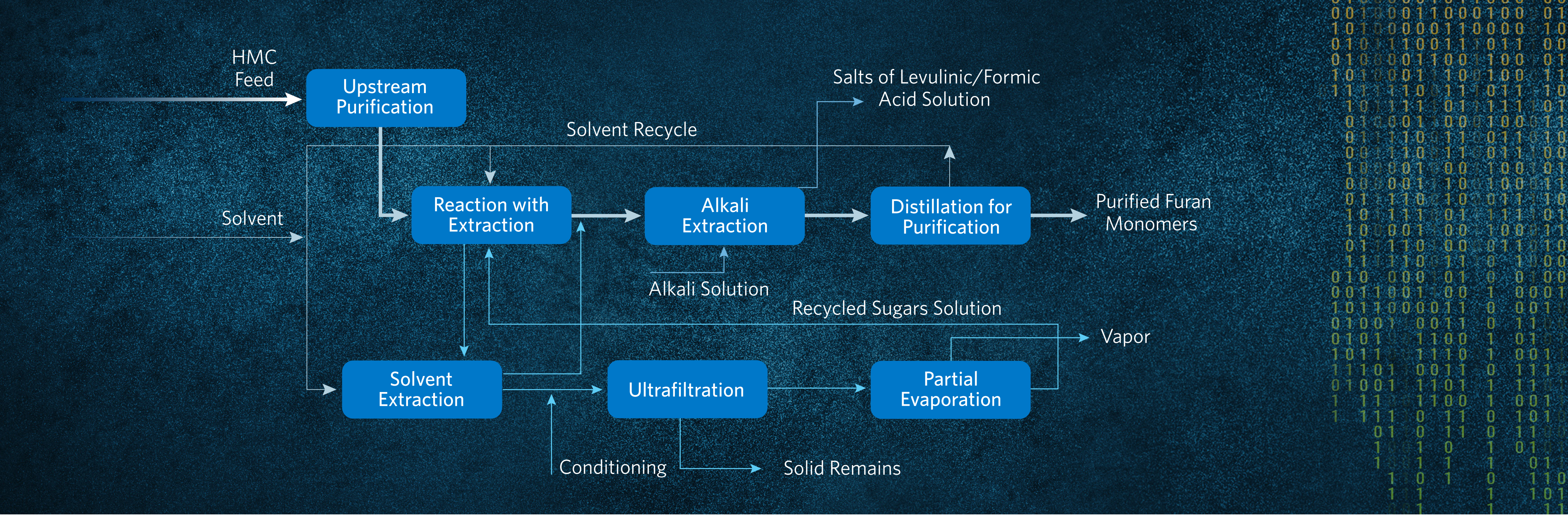
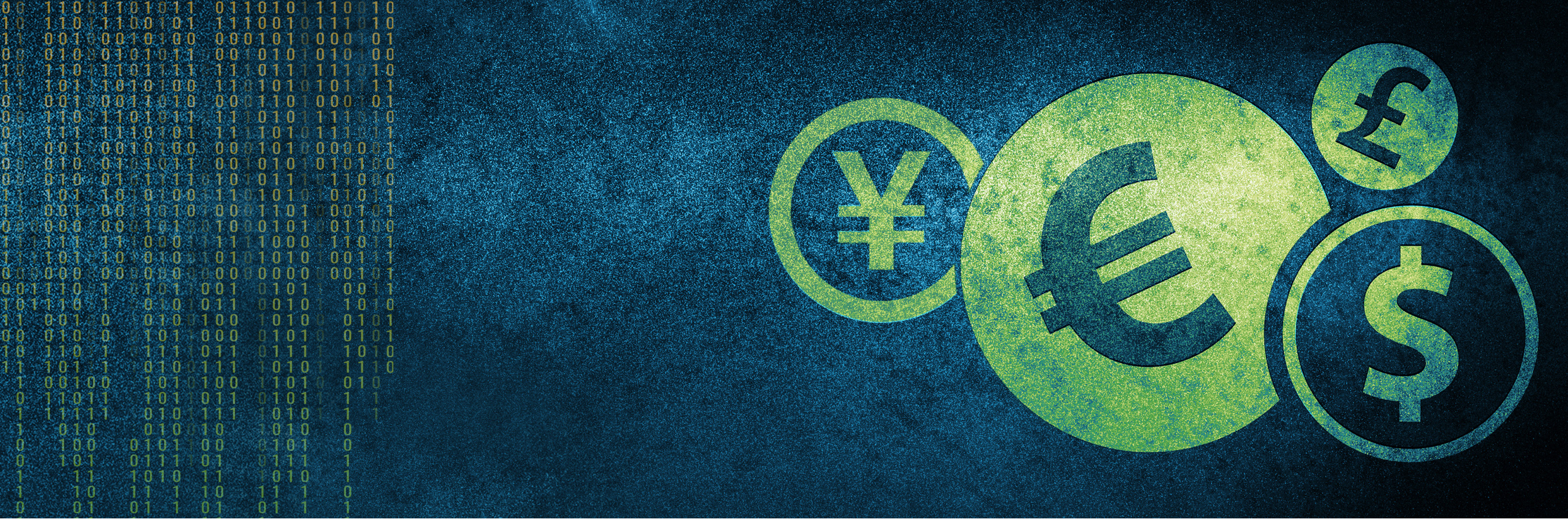



Figure 4. BioSprint process to convert hemicellulose to furan monomers.

## Scale Up and Economic Evaluation of Bioprocesses

One of the main roles of digital solutions in bioprocessing is to build scale-up models. These models demonstrate whether a process is technically or economically feasible and what the CAPEX/OPEX implications of the project are. The scale up models can shorten R&D time by allowing testing for a variety of feedstocks and processes and by predicting yields or energy and process needs.

BioSprint is a project led by a European consortium of research and commercial partners. The goal of the project is to purify and convert hemicellulose to produce fossil-based alternative polymers. Figure 4 displays the overall process diagram of their design. The project uses a combination of laboratory generated data along with simulation models to verify feasibility and the best design to get the highest conversion yield. For example, the effects of feed concentration, temperature, homogeneity or heterogeneity of catalyst, yield vs. residence time, and pretreatment options have all been evaluated using Aspen Plus models. The data were then fed to Aspen Process Economic Analyzer™ to estimate the required CAPEX and OPEX investments. Process simulation helped the team to improve quality and speed of R&D, design unconventional unit operations and identify technology limits.



# Conclusion

Despite the greater push for sustainable fuels and chemicals, design and scale-up of biofeedstock processing remain challenging. Any new process has to successfully account for complex molecular level components of the feedstock as well as for methods to extract, transform and purify desired products. While experimental research can shed light on some of these complexities, ultimately digital solutions are needed to scale processing or evaluate economic feasibility. AspenTech Performance Engineering with its extended library of compounds and frequently updated models can complete fundamental R&D efforts, and reliably model new bio-based processes in a fraction of the time to ensure feasibility and return on investment.

**Citations:**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## About Aspen Technology

Aspen Technology, Inc. (NASDAQ: AZPN) is a global software leader helping industries at the forefront of the world's dual challenge meet the increasing demand for resources from a rapidly growing population in a profitable and sustainable manner. AspenTech solutions address complex environments where it is critical to optimize the asset design, operation and maintenance lifecycle. Through our unique combination of deep domain expertise and innovation, customers in capital-intensive industries can run their assets safer, greener, longer and faster to improve their operational excellence.

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