Proprietary process technology

PROESA®

Ethanol Production from Biomass

CELLULOSIC ETHANOL TECHNOLOGY

versalis

Versalis proprietary process technologies available for licensing

Our company

Versalis (Eni) is a dynamic player in the chemical industry which prides itself on competence and technologies such as to meet multifaceted and ever-evolving market needs.

As a European manufacturer with more than 50 years of industrial and commercial history, Versalis stands as a complete, reliable and now global supplier in the basic chemicals, intermediates, plastics and elastomers markets with a widespread sales network.

Relying on continuous development and strengthening the management of the knowledge gained through its long-lasting industrial experience, Versalis has become a global licensor of its proprietary technologies and catalysts. The strong integration between R&D, Technology and Engineering departments, together with a consolidated market acumen, are key strengths to finding answers to customers' requirements.

Our commitment to excellence, quality of our products and services, makes our company an active partner in the growth of our customers. Through engineering services, technical assistance, marketing support and continuous innovation, our knowledge makes the difference in customizing any new project throughout all phases.

Customers can rely on this strong service-oriented outlook and benefit from a product portfolio that strikes a perfect balance of processability and mechanical properties, performance and environmentally-friendliness.

Versalis is committed to reinforce its competitive position with regards to chemistry from renewables, merging its new activities into a dedicated business unit and developing an integrated technological platform in line with the company's business strategy.

Introduction to Versalis PROESA® cellulosic ethanol technology

Advanced biofuels, such as cellulosic ethanol, have been worldwide identified as key components in the decarbonization of the transport sector and an increasingly number of policy framework are promoting their deployment at a large scale.
The PROESA® technology has been developed from 2006 to target the growing advanced biofuels market and the results obtained from the pilot plant built in Rivalta Scrivia (Italy) constituted the basis for the design of the commercial-scale facility in Crescentino (Italy) that has been in operation since 2013.
This 22 kt/y facility is designed to process a variety of locally available cellulosic feedstock (i.e. arundo donax, wheat straw and rice straw). Crescentino plant has steadily improved process performance in terms of capacity and stability, being an extraordinary tool for detection and resolution of process issues emerging only at industrial scale, thus making PROESA® the only cellulosic ethanol technology proven at such a scale.

Key Features of PROESA® technology

- Flexibility toward different feedstock;
- A steam based technology, without chemicals addition in the pretreatment of biomass, that allows a simple metallurgy for equipment;
- Proprietary know-how covered by an extensive number of patent and patent applications;
- C5 and C6 sugar extraction and co-fermentation;
- Perfect fitting to agrochemical industry, with a very low environmental impact;
- Crescentino industrial plant as reference.

R&D

PROESA® was developed by a group of researchers at the R&D Center in Rivalta Scrivia (Italy). Operations began in 2006 and continued during the following years, bringing to the construction of a pilot plant (in operation since 2009), on which the lab results were tested to ascertain the flexibility of the process. It was only after the validation of the results obtained on the pilot plant that it became possible to apply the technology on industrial scale at the Crescentino plant.
PROESA® is currently being commercialized for the production of bioethanol via fermentation of cellulosic sugars. However, another key feature of the technology is the potentially achievable high purity fermentable sugar stream. This advantage makes PROESA® suitable for both biological and chemo catalytic technologies currently under development for the conversion of sugars to highvalue bio-based chemicals and further advanced biofuels.

Process design

Process design is flexible and able to face different conditions and constraints. Each project is individually evaluated to offer the best solution, tailored to specific customer's need. The valuable experience gained during Crescentino start up and developments is regularly transferred to new projects.

Mechanical design

The collaboration between researchers and engineers has allowed to develop unique and well sound engineering solutions for critical equipment that guarantee the best results in term of mechanical reliability and process performance.

Industrial Application

The industrial unit located in Crescentino (Italy) represents the world's first commercial scale cellulosic ethanol plant. The plant includes a bioethanol production train, a power plant operated at 13 MWe and a biogas generation unit integrated with waste water treatment. The energy produced is used to power the plant and the quantity in excess is sold to the national power grid.
The feedstock used so far in the plant are wheat and rice straw, arundo donax and hardwood.
In addition to Crescentino, PROESA® technology has been licensed to other two plants, in Brazil and Slovakia.

Cellulosic ethanol production using PROESA®

The overall project development of a cellulosic ethanol production plant includes several aspects that need to be considered such as biomass supply chain, lignin valorization and water recirculation / management
The capital cost of a PROESA® cellulosic ethanol plant depends on a number of factors including capacity, location, project scope (e.g. feedstock handling, utility requirements, client specific requirements, product specifications, etc.) and contracting / implementation strategy.

The OSBL (outside battery limit) portion of the project will be site and client specific.
The major operating expense for a PROESA® facility is usually the biomass. One of the advantages of PROESA® is the high feedstock flexibility, which is key in designing a cost-effective supply chain tailored to the specific location. Guaranteed conversion yield (biomass - to - ethanol) will depend on a number of parameters, most importantly the composition of the chosen biomass in terms of fermentable sugars: as a general reference, such yield might range between 5 ÷ 6 tons of dry biomass per ton of bioethanol.
Versalis cooperates with biotech partners – for cellulosic enzymes and for the 2G sugars fermentation microorganism – in order to offer to PROESA® licensees performance guarantees and price competitiveness for the biocatalysts required by the PROESA® process.
It is worth to be mentioned that the energy content of the lignin generated as by-product is in excess of the energy requirements of the process itself (steam and electricity). The ability to monetize this surplus by selling the excess energy or the lignin itself to third parties is a key success factor.

Process description

The core of the PROESA® technology is an integrated and chemicals-free pretreatment, followed by viscosity reduction and enzymatic hydrolysis steps that prepare 2G sugars for fermentation to bioethanol.

Biomass pretreatment

The Versalis proprietary pretreatment process consists of a "smart" cooking step. Depending from the biomass and the cleanness guaranteed by the supplier, the feed handling may include a soaking section to remove debris and impurities. The process then utilizes saturated steam to disrupt the bonds between lignin, cellulose and hemicellulose. The technology maintains the principal advantages of standard steam and water based processes (no chemical addition and high efficiency separation of cellulose and hemicellulose) while reducing the formation of inhibitors to the downstream processes. The net effect of these processes is a reduction in capital (simple materials of construction) and operating costs (low enzyme dosage). The major advantages of the pretreatment concept are:

- Minimum requirement for feedstock size reduction: no grinding or size reduction other than primary shredding of bales or chopping
- High feedstock flexibility: ability to process a wide variety of lignocellulosic feedstock, such as energy crops (napier grass, miscanthus, energy cane), agricultural and industrial residues (wheat and rice straw, corn stover, sugar cane bagasse, tops and leafs), and hard wood species (poplar, chestnut, eucalyptus)
- No chemical addition (useful to avoid expensive construction materials and neutralization operations)
- Optimization of process conditions to maximize yield using a wide range of biomass composition, moisture content, size and density
- Limited formation of inhibitory compounds and degradation products
- High accessibility / digestibility of pretreated material to enzymatic hydrolysis

Viscosity reduction and enzymatic hydrolysis

PROESA® uses an efficient liquefaction of the pretreated material to ensure a constant and continuous flow of material to the fermentation section. Enzyme action coupled with a unique process design allows for liquefaction with very short residence times and high dry matter contents.
The major advantages of the enzymatic hydrolysis concept are:

- State-of-the-art design that leads to an easy scale up
- Very low energy consumption for mixing due to Versalis' proprietary configuration
- Easy pH and temperature control
- Adjustable degree of hydrolysis, suitable for a wide variety of sugar conversion platforms

Fermentation and lignin separation

The yeast used in the process is capable of co-fermenting C5 and C6 sugars and it is propagated at site. The current generation of yeast is able to tolerate the presence of naturally generated acetic acid. Subsequently, the ethanol is recovered by distillation plus molecular sieve dehydration. Lignin water slurry is recovered at the bottom of stripping unit and sent to lignin recovery and valorization.

PROESA® Advantages

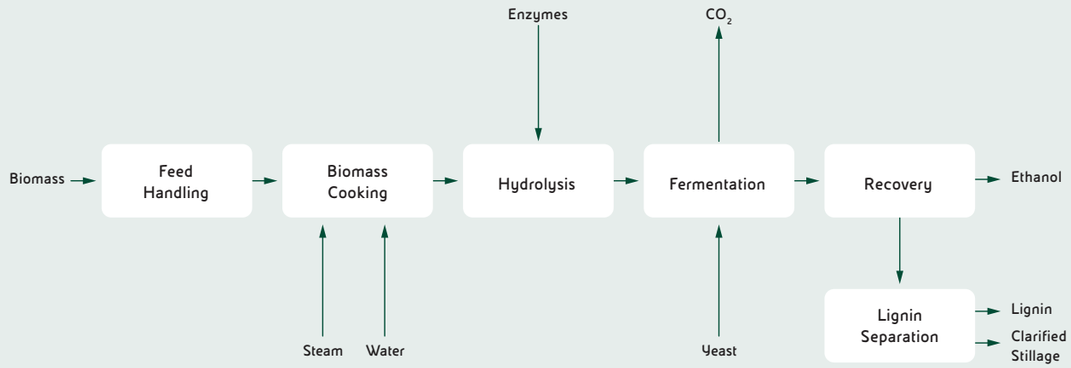
The PROESA® technology offers significant advantages over competing technologies for the conversion of non-food cellulosic biomass to ethanol and other biofuels and bio-based chemicals, being:

- Flexible – in terms of feedstock and therefore siting
- Proven – at commercial scale
- Competitive – combination of low capex and opex
- Guaranteed – backed by performance guarantees on critical parameters
- Sustainable – Versalis is committed to continuous improvement in order to remain industry leader and deliver further value to its customers.

Plant in Crescentino (Italy)

fig. 1

PROESA® Process



Proprietary process technologies portfolio

Biotech

PROESA® 2G Ethanol and Cellulosic Sugars

Phenol and derivatives

Cumene (with PBE-1 zeolite based proprietary catalyst)*
Phenol, Acetone, Alphamethylstyrene*
High selectivity Cyclohexanone
Acetone hydrogenation to Isopropyl Alcohol*
Isopropyl Alcohol to Cumene*
Ammoximation (with Titanium silicalite based proprietary catalyst TS-1)

DMC and derivatives

Dimethylcarbonate (via Carbon Monoxide and Methanol)*
Diphenylcarbonate*

Proprietary catalysts

Titanium silicalite
PBE-1 Zeolite
PBE-2 Zeolite

Styrenics

Ethylbenzene (with PBE-1 and PBE-2 zeolite based proprietary catalyst)
Styrene
GPPS
HIPS
EPS suspension polymerization
ABS continuous mass polymerization
SAN

Polyethylene

LDPE
EVA

Elastomers

Emulsion-SBR
HSL Latices
Solution-SBR
SBS
SIS
LCBR
HCBR
NBR
Carboxylated latices
EP(D)M

* Co-licensing in cooperation with Lummus Technology (a McDermott International Company.
** Close to commercialization.

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01-2019