CHEMSYSTEMS
PERP PROGRAM

Report Abstract

"Green" Polyethylene
PERP06/07-S11

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"GREEN" POLYETHYLENE

There is no hard and fast definition of a "green product", and this bio-based polyethylene does not meet one typical goal of green products since the polyethylene product is not biodegradable. Nonetheless, for the purposes of this report since the feed is renewable, it is referred to as "green" polyethylene.

The primary route used to make "green" polyethylene is via the production of ethanol. Dow Chemical and Braskem, independently have plans to build large-scale projects in Brazil which would produce polyethylene from ethylene based on renewable ethanol from sugarcane. Additionally, Borealis has announced plans to expand its production of ethylene in Sweden, by using bioethanol as a raw material.

This ChemSystems PERP report details the current ethanol technologies and potential second generation approaches, including:

- Fermentation of sugar, starch, and grain substrates
- Various leading developments in fermentation of lignocellulosic biomass

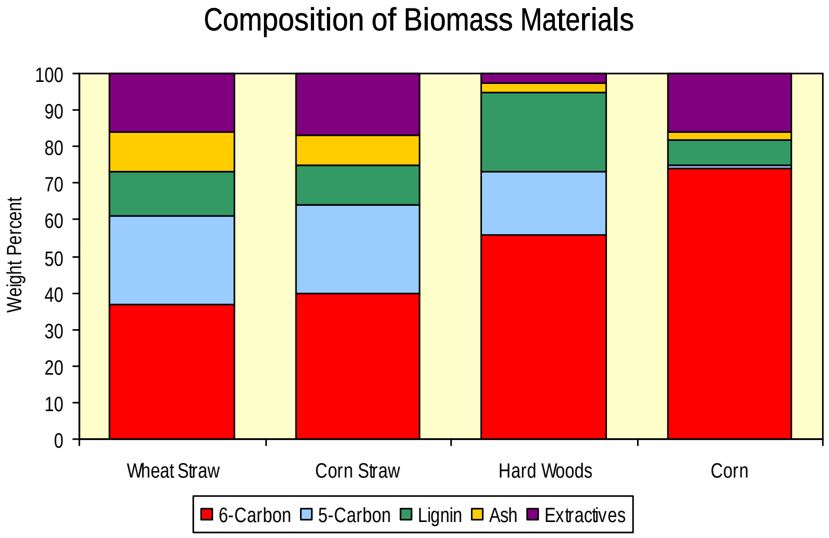
In addition, a discussion of the Scientific Design ethanol dehydration technology to produce ethylene (the rights to which are currently owned by Chematur) is included.

An alternate route to "green" polyethylene via gasification of biomass to produce syngas, followed by synthesis of methanol and methanol-to-olefins (MTO) is also detailed.

As well as these technologies, some of the economics and other topics discussed in this report are highlighted below.

ETHANOL

Ethanol, whether used for fuel, as a chemical, or a beverage, is being produced almost exclusively by the fermentation of sugars. The source of the sugar can be sugar cane, grapes, starch grains like corn, or, potentially, biomass. The process of producing the sugars becomes more difficult as one moves from sugar cane to biomass, because biomass is composed of cellulose, hemicellulose, lignin, ash and soluble substances called extractives. Cellulose and hemicellulose make up the majority of the dry weight of most biomass materials. Cellulose is a polymer of glucose and is difficult to break down into glucose because of its crystalline structure. Hemicellulose is composed of several different sugars including the six-carbon sugars glucose, galactose, and mannose, and the five-carbon sugars arabinose and xylose. Hemicellulose is more easily broken down into its individual sugars. Lignin is a complex phenolic material that acts as glue to hold the cellulose and hemicellulose together. Extractives can have an economic value depending on their characteristics and cost of recovery. The figure below shows the composition of corn and several biomass materials that have been investigated for conversion to ethanol fuel.



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Enzymes and Other Factors in Bioethanol production from Starch and Sugars Biomass Sources

Improved enzymes have the potential to significantly improve the economics of bioethanol from grains, other starch sources, and sugars, and they remain a key determinant of economic feasibility for biomass-to-ethanol.

Development of an improved ethanologen (ethanol producing organism) can help significantly increase the volume of feasible ethanol production from grains and sugars and enable the development of biomass to ethanol.

Novozymes, Genencor, Verenium and Iogen are currently developing enzymes to improve ethanol production.

Plant (feedstock crop) biotechnology also has a major role in improving the feasibility, economics and robustness of liquid biofuels production; this is covered in other sections of this report.

Enzymes and Other Factors in Bioethanol production from Lignocellulosic Biomass Sources

Biomass (cellulose/hemicellulose) fermentation will need to compete with thermochemical routes for producing liquid biofuels. There are fundamental challenges in converting cellulosic biomass to liquid biofuels, whether by enzymatic or thermochemical routes, and even more for fermentation routes. Some of these are:

- Availability of inexpensive feedstock
- Storage of feedstock (which is often seasonally produced), without degradation for continuous feeding to the process over the year
- Transport of feedstock to the processing facility
- Physical treatment of feedstock (cleaning, milling, chopping, and grinding)
- Obtaining a sufficient volume of biomass feedstock at one site economically
- Reliable and efficient conversion of feedstock to fuel.

Because lignocellulosic biomass is designed by nature to be recalcitrant to the enzymatic attacks mounted by life forms in the environment that would feed on it, pretreatment technologies need to be used to overcome this recalcitrance to reduce the difficulties and costs of subsequent steps. A range of pretreatment technologies (dilute acid, organic solvents, steam explosion, ammonia fiber explosion - AMFE or AFEX, and so on) to disrupt the hemicellulose/lignin sheath that surrounds the cellulose in plant material are available. Each of these technologies has advantages and disadvantages in costs, yields, material degradation with respect to subsequent processing objectives, other downstream processing impacts and needs, and generation of process wastes.

The National Renewable Energy Laboratory (NREL), has recently and significantly co-funded and collaborated with the private biotech companies Novozymes and Genencor to advance the biotechnology related to the efficacy and cost of enzymatically converting biomass to sugars and next to ethanol.

Other organizations are reported to be researching lignocellulosic-based ethanol production via fermentation routes or planning projects based on various types of biomass, including Iogen (Canada/United States), Dedini (Brazil), Abengoa Bioenergy (Spain), and BCI (United States).

ETHYLENE VIA ETHANOL TECHNOLOGY

The chemistry of ethylene production via dehydration of ethanol can be represented by the following reaction:

$$CH_3CH_2OH \longrightarrow CH_2{=}CH_2 + H_2O$$

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The dehydration reaction is carried out at elevated temperature over a specially treated catalyst. High purity and yields are obtained. A conventional purification scheme may be used to remove trace by-products.

The conversion of ethanol to ethylene can take place in either a fixed-bed or fluid-bed reactor. The fixed-bed route is licensed by Chematur Engineering AB and is presented herein. Lummus has developed a catalyst and process for the dehydration of ethanol to ethylene utilizing fluidized-bed technology.

ETHYLENE VIA BIOMASS GASIFICATION TECHNOLOGY

An alternative route to "green" polyethylene gasifies biomass (e.g., wood, switchgrass) to produce syngas along with steam and power co-generation. Biomass gasification has perhaps the most potential for feedstock flexibility and improved conversion economics as well as for extending product capabilities. The syngas is used to generate methanol, which is sent to a methanol-to-olefins unit (MTO) and the ethylene produced therein is polymerized to LLDPE or HDPE.

It should be noted that in addition to the biomass mentioned herein, bio-methane can also be used as feed. Bio-methane typically contains a high concentration of carbon dioxide.

Methanol technology (reforming, synthesis & distillation) is licensed by a number of companies. The synthesis & distillation processes are typically licensed by one supplier, while another supplier is chosen for the reformer.

MTO commercially available technologies include UOP/HYDRO, for which a detailed process description is given in this report. Technology is also available from Lurgi, and the Dalian Institute of Chemical Physics (DICP). DICP is close to commercializing its own technology.

ECONOMIC & COMMERCIAL ANALYSIS

In this section, the cost of production for ethanol are provided for both corn-based (dry milling) and sugarcane-based fermentation. The costs of ethylene are then examined via ethanol dehydration and compared to ethylene via conventional ethane steam cracking. A speculative thermochemical approach to ethylene is also looked at involving gasification of biomass to synthesis gas, conversion of the synthesis gas to methanol and then finally converting methanol to olefins using UOP's MTO process. Lastly, the economics of converting the ethylene, using the costs of all of the above routes, to "green" and conventional polyethylene are developed and compared.

A discussion on the commercial impact of the ethanol feedstock supply and region where production takes place (USA, Canada, Brazil, EU, India, China, Australia, Central & Latin America) is given.

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