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Green Propylene

Process Technology (including Bio-ethanol, Bio-butanol, Bio-diesel, Biomass, and Vegetable Oil Routes), Production Costs, and Regional Supply/Demand Forecasts are presented.

PERP07/08S11

Report Abstract

April 2009

Nexant

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INTRODUCTION

This report discusses several routes to producing a "green" propylene product. (While this is strictly not a green product since the propylene product is not biodegradable, for the purposes of this report since the feed is renewable, it shall be referred to as "green" propylene.)

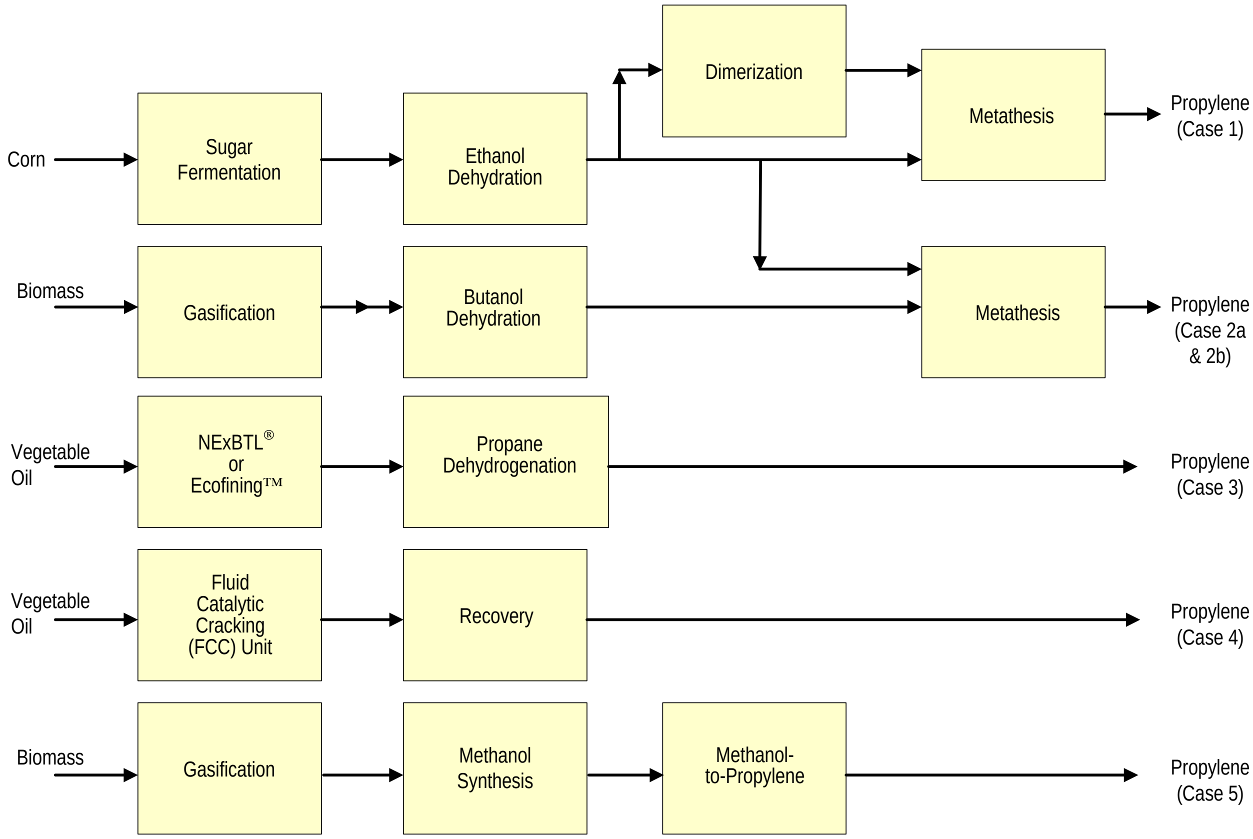
The discussion and analysis herein of green propylene is not to be confused with Biopropylene™. Cereplast, Inc. is the manufacturer of this proprietary bio-based sustainable plastic with properties equivalent to polypropylene. This hybrid resin replaces fifty percent or more of the petroleum content used in traditional plastic resins with bio-based materials such as starches from corn, tapioca, wheat, and potatoes.

Several cases are considered herein for the production of green (or sustainable) propylene. These include:

- Case 1: Fermentation of sugars to produce bio-ethanol is followed by dehydration to bio-ethylene. A portion of the ethylene is dimerized to produce normal butenes. The bio-butenes are then reacted with the remaining bio-ethylene via metathesis to produce green propylene. Butene-1 is isomerized to butene-2 (both *cis* and *trans* isomers) in the latter reaction.
- Case 2: Butanol is produced either by fermentation of sugars (Case 2a) or gasification of biomass (Case 2b) and the bio-butanol is dehydrated to produce bio-butene. The bio-butene is reacted with bio-ethylene as above.
- Case 3: Bio-propane produced as a by-product of biodiesel is dehydrogenated to produce green propylene.
- Case 4: Vegetable oil is fed to an enhanced fluid catalytic cracker (FCC) unit to produce green propylene.
- Case 5: Gasification of biomass to produce a syngas is followed by synthesis of bio-methanol. Green propylene is then produced via methanol-to-olefins technology.

A simplified block flow diagram of the cases considered herein is shown in the figure below.

Routes to "Green" Propylene



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Globally, the biofuels industry is facing multiple aspects of a crisis most commonly termed "food versus fuel", indicating the conflict in many local economies and in the global economy stemming from using easily converted starch, sugar, and natural oils and fats resources, and/or the land and water resources needed for their production, to make biofuels. The concern is making them unavailable or too expensive for food and animal feed markets. The press sometimes makes more of this problem than actually exists. While biofuels are making demands on food-related resources, the demand for these commodities has increased dramatically with the growth of China and other Asian and developing economies. Many of these populations are demanding and can afford more high-quality food of all kinds in their diet. This growth also has contributed to driving up agricultural commodity and food prices. Much of the crisis is manipulation by food producers, the press, and others. In fact, even at current high costs per bushel, the corn cost in a typical box of corn flakes, for example, is about one percent of the grocery shelf price. Another type of concern is environmental, such as the reaction of environmental groups, the press, and the public to the perception of destroying tropical rainforests to develop additional oil palm plantations, not for food, but to supply demand in Europe and elsewhere for biodiesel production. In either case, perception may be as important as fact, and pressure is felt by all stakeholders in the biofuels area to find alternatives to using food and/or agricultural land for biofuels. Therefore as an alternative to using corn or soybean as feed for producing green propylene, two processes using biomass (wood chips) and gasification technology were included in the analysis that is given in the report.

Agricultural, forest, and consumer waste biomass has great potential as feedstock for biomass production, but faces substantial challenges to commercialization. When considering biomass feed sources, it is important to consider which feed streams have the best characteristics of:

- proximity to processing
- infrastructure concerns, including moisture level, volume, potential field degradation, contamination with microbes
- consistency of physical characteristics of feedstock
- supply size and stability of feedstock.

The technologies employed in this analysis are discussed in more detail under Technology Analysis (section 2). Section 3 of this report analyzes the economics for producing green propylene via these various routes. Section 4 reviews the commercial aspects of propylene.

TECHNOLOGY ANALYSIS

Route via Bio-Ethanol (Fermentation, Dehydration, Dimerization, and Metathesis)

This route to green propylene includes fermentation of sugars to produce bio-ethanol followed by dehydration to ethylene. A portion of the ethylene is dimerized to produce normal butenes. The butenes are then reacted with the remaining ethylene via the metathesis reaction to produce green propylene.

- Ethanol fermentation via sugarcane fermentation and other sugar and starch substrates is discussed including subsections describing:
  - Whole-kernel dry milling process

  Technology advances for corn dry milling and corn wet milling are also briefly mentioned.
- Ethylene via ethanol dehydration is discussed. The use of ethanol to make ethylene on a comparatively small scale is well established in developing countries not having ready access to hydrocarbons. 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 315-425 °C (599-797 °F) over specially treated activated alumina catalyst. The ethylene is obtained in yields of approximately 96 percent. However, ethanol obtained from ordinary biomass resources can contain many impurities other than water and these impurities themselves or their decomposition products can contaminate ethylene when the ethylene is produced by a dehydration reaction, which in turn adversely affects the metathesis catalyst downstream. The process is described in more detail in the report including a process flow diagram for Chematur's fixed-bed, ethanol-based ethylene plant.

  Ethanol dehydration via conventional FCC is briefly mentioned.

- Phillips Petroleum Company invented an olefin dimerization process for the production of normal butenes and this technology is now licensed by Lummus Technology Inc. The dimerization process is illustrated with a process flow diagram and described in the report.
- Olefin interchangeability presents a classic problem of the petrochemical industry. The major source of olefins - ethylene, propylene, and C_4 unsaturates - is steam cracking of hydrocarbon fractions, varying from ethane to gas oil. C_3 and C_4 olefins are also produced by catalytic cracking, but in streams that are more dilute. Steam cracking is a free radical reaction in which beta-scission predominates; thus ethylene is the major product regardless of the chain length of the starting material. C_2, C_3 and C_4 olefins ratios can be controlled somewhat by cracking severity. However, this control is rarely adequate to accommodate the demands of the marketplace. Also, there is frequently no discretion relative to what is cracked. A cracker in a gas-rich region will crack ethane and/or propane and will be limited by the amount of higher hydrocarbons available.

  Olefin metathesis, or disproportionation, provides an opportunity to achieve olefin interchangeability. The chemistry and process design are outlined in the report, in particular, Lummus' Olefin Conversion Technology (OCT) including process flow diagram is described.

Routes via Bio-Butanol

Two routes are considered for producing green propylene employing bio-butanol. The first is fermentation of sugars to form bio-butanol, followed by dehydration of the butanol to butenes. The bio-butene is then reacted with bio-ethylene to form green propylene via metathesis. The second route is to produce bio-butanol via biomass gasification. Each route is discussed in more detail below.

- Bio-butanol is different from bio-ethanol primarily because its history is far shorter and different, not being grounded primarily in beverage and fine chemicals manufacturing as was bio-ethanol. The fermentation routes for both went through similar replacements by the respective synthetic, petrochemical-based products for much of the latter 20th Century, but fermentation bio-ethanol (sugar and grain-based) remained an important beverage product (beer and distilled beverages) throughout. Therefore, bio-butanol technology developers are more likely associated with chemical and biotech process development than have been technology sources for conventional production. Additionally, the generally bacteria-based fermentations for bio-butanol appear to be more fundamentally and directly applicable to cellulosic feeds (e.g., Blaschek et al. *C. beijerinckii* BA101's high conversion of pentoses) than the yeast-based ethanol fermentations.
  - In particular, *C. beijerinckii* - based fermentation is discussed in the report.
- Mitsui has developed a process to convert the acetone produced during the production of phenol to propylene for recycle to a cumene plant upstream. This technology could easily be applied to convert the by-product acetone produced during the fermentation process to additional green propylene. Chemistry, process flow diagram and description are outlined in the report.

- Biomass gasification to produce bio-butanol, and bio-butenes via dehydration of bio-butanol are briefly discussed.

Route via Biodiesel (Nexbtl® Or Ecofining™)

In this case propane produced as a by-product of biodiesel (also called green diesel) is dehydrogenated to produce green propylene.

- Neste Oil's NExBTL® renewable diesel technology (which stands for "Next Generation Biomass-to-Liquid") is discussed in the report.
- UOP and ENI have developed a technology for converting vegetable oils to renewable diesel ("Green Diesel"). The Ecofining™ process hydrogenates triglycerides and/or free fatty acid feedstocks such as pretreated vegetable oils (e.g., rapeseed, canola, soybean, palm, and jatropha) and animal fats (e.g., tallow). A simplified flow diagram and brief discussion of the process is given in the report.
- Propane dehydrogenation technology is a derivative of light paraffin dehydrogenation. The origin of the some technologies discussed here had been isobutane dehydrogenation. However, the current generation systems are an adaptation from butadiene production units. Chemistry is given and discussed, as well as a tabulated summary of the process characteristics of the various propane dehydrogenation technologies.
- Many companies now market or have developed high severity or enhanced FCC-type processes for the purpose of increasing propylene yields and a few have expanded the feeds to include vegetable oils. UOP's PetroFCC™ technology, Shell's MILOS technology, and Petrobras' High Olefins FCC technology have published yield data for cracking vegetable oils.
  - UOP has leveraged its FCC experience and know-how to develop and license a new type of cracking process. PetroFCC™ process is described including a discussion of RxCat™ technology and PetroFCC™ process yield structure.

  Petrobras'high-plefins FCC process is also briefly discussed.
- Syngas is produced via gasification of biomass. The syngas is used to produce bio-methanol followed by synthesis of green propylene via Lurgi's methanol-to-propylene (MTP) technology. Biomass gasification, methanol synthesis and methanol-to-propylene including Lurgi's Mega Methanol™ process are briefly discussed. Other gasification routes being developed are also briefly discussed.

ECONOMIC ANALYSIS

For Case 1 outlined in the introduction, the following cost of production estimate tables have been developed:

- Bio-Ethanol via Fermentation (of corn) Process
- Bio-Ethylene via Dehydration Process
- Bio-Butenes via Dimerization Process:
- Green Propylene (Polymer Grade) via Metathesis Process

Similarly, a series of cost of production estimate tables have been developed for each of the cases (2a, 2b, 3, 4, and 5) outlined in the introduction.

In addition, the sensitivity of the economics for producing green propylene has been developed for feed price, capital investment, and economy of scale.

As discussed in this report, there are many potential routes to green propylene. And, as also shown in this report, these routes all give a different set of cost of production economics. However, in assessing the merits of the various approaches, process economics are the not the only criteria. These routes all vary with respect to feedstock (food crop versus bio-waste), process complexity (number of steps), and experience (commercially used process steps versus steps still needing development). All of these factors are summarized in this section for the six cases presented.

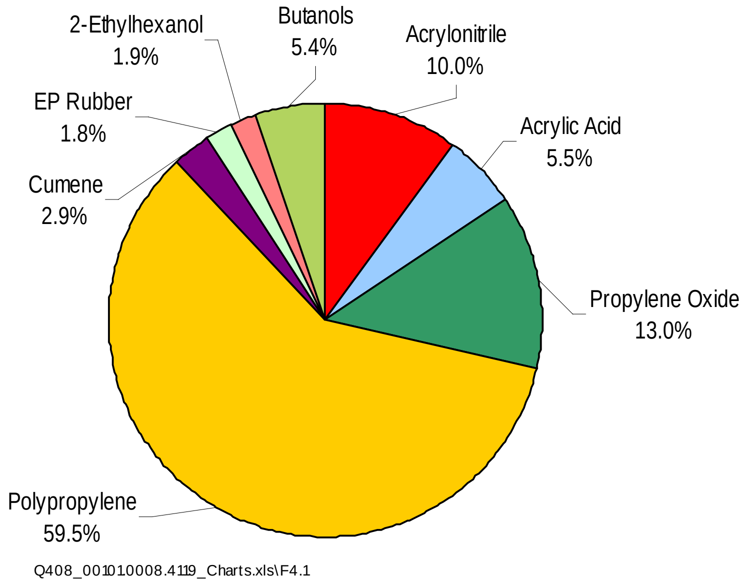
COMMERCIAL ANALYSIS

Propylene demand is approximately one-half the size of ethylene demand, is the second most important olefin product, and like ethylene is a primary petrochemical precursor. In each region polypropylene is the largest propylene derivative.

Propylene oxide is used in rigid foam applications such as building insulation, and demand therefore tracks the performance of the construction industry and general economic conditions. Propylene oxide also has applications in the production of polyols for polyurethanes and propylene glycol. Other uses of propylene are briefly outlined.

A chart of propylene end-use demand for the U.S. is shown in the figure below.

U.S. Propylene End-Use Pattern



- Regional supply, demand and trade data are given and discussed for the United States, Western Europe and Asia Pacific
- Extensive tables showing propylene capacity by company, process type (metathesis, steam cracker, FCC etc), specific plant capacity & its location, is given for each of the regions discussed.

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