Originally appeared in:
August 2009, pgs 65-68.
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HYDROCARBON PROCESSING®

Biorefineries: Fact or fiction?

Technology advances facilitate building integrated chemical complexes based on renewable feedstocks that can cost-effectively process ethylene derivatives

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Integrated complexes for petroleum-derived processes are common. However, the same types of complexes are not typical for processes based on bio-renewable feedstocks. New technology advancements overcome processing hurdles that allow cost-effective production of ethanol-derived ethylene derivatives that can compete with traditional processing methodologies.

Background. Over the last 90 years, feedstocks for most downstream petrochemicals are petroleum based. Due to rising prices of crude oil and concerns over the environment, renewed interest for applying alternative feedstocks—in particular, bio-renewable feedstocks—has emerged. Among the many bio-derived feedstocks, ethanol has received the most interest. Ethanol production is based on fermenting readily available agricultural products such as sugar cane and corn. Fermentation technology is simple and commercially developed and can be easily transferred to less developed nations.

During the 1950s and 1960s, ethanol was largely used to produce commodity chemicals in Brazil, India and Australia due to:

- Locally available, fermentable agricultural materials
- Lack of indigenous hydrocarbon feedstock resources.

New ethanol technologies. Following a decline in interest, the ethanol-based industry staged a comeback during the energy crisis of the early 1970s as a possible option to reduce dependence on foreign oil imports. During this time, a fully-integrated ethanol-to-ethylene glycols process was developed as an alternative to petroleum-based feedstock for glycols production. In 1989, the first commercial plant using this integrated technology was commissioned in India in 1989. This facility was expanded several times over the last 19 years; it is currently producing ethylene oxide (EO)/ethylene glycol (EG) from ethanol derived from molasses.

In Brazil, more than 30 products were derived from ethanol, several with installed capacities above 100,000 tpy during this period. However, as naphtha prices declined throughout the 1980s and 1990s, the production for many ethanol-based chemicals became uneconomical. As the price of oil increased recently, interest in ethanol-derived chemical processes renewed. Other interesting reasons for ethanol-based chemicals include:

- Significant productivity improvements and cost reductions in ethanol production from technology evolution
- Increasing availability of fuel ethanol, with ambitious expansion plans in the US and Brazil
- Promise of an ethanol-production process that is both cheaper and larger volume based on cellulose biomass such as sugarcane bagasse
- Environmental concerns
- Energy supply security issues.

Global supplies. Fig. 1 shows worldwide ethanol production for 2006. Due to the renewed interest in ethanol, worldwide ethanol production is projected to more than double over the next 15 years to a worldwide capacity of more than 120,000 million liters by 2020, as shown in Fig. 2. The main reason for ethanol production expansion, especially in the US, is its use as an octane additive for gasoline. As oil prices rise, emphasis will shift toward

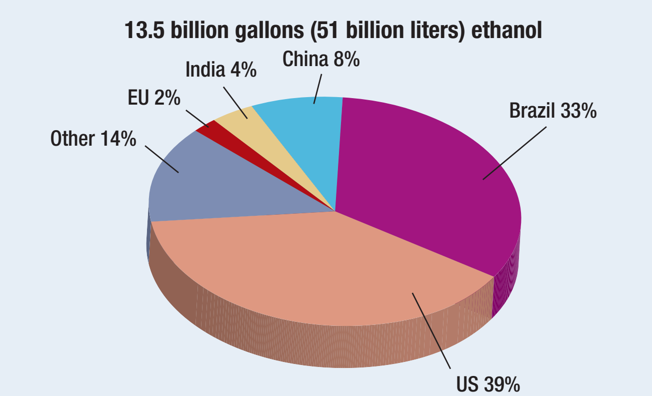

FIG. 1 Worldwide ethanol production in 2006.[1]

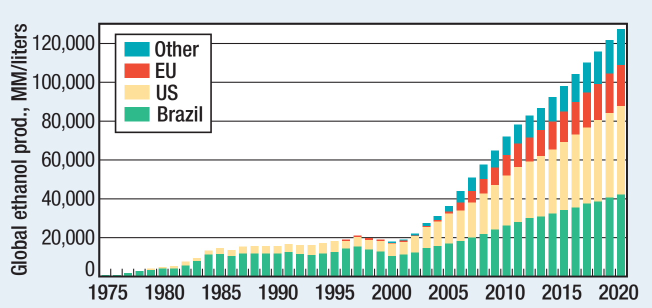

FIG. 2 Expansion of global ethanol production capacity—1975 to 2020.[2]

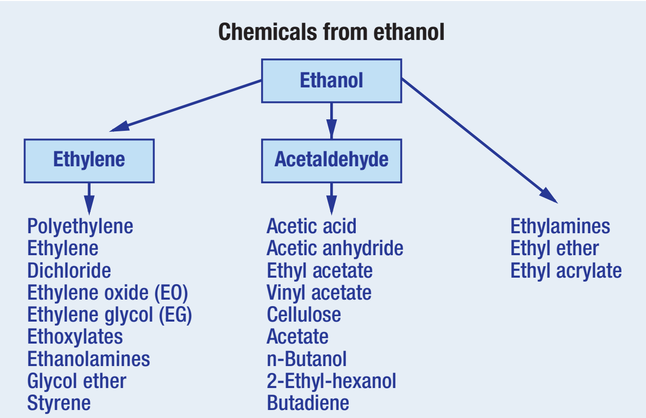

FIG. 3 Chemicals that can be produced from ethanol.[1]

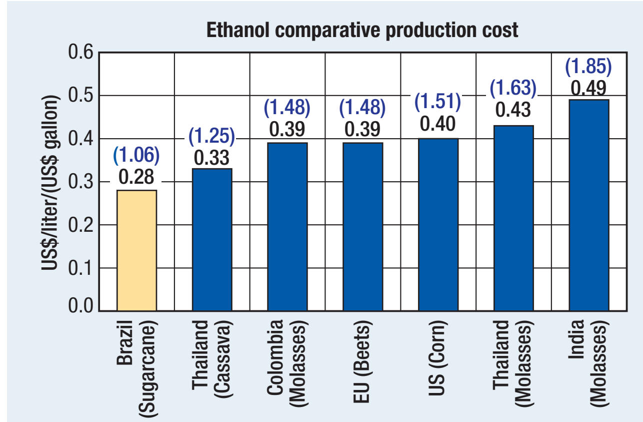

FIG. 5 Ethanol production cost by various nations and feedstocks.[3]

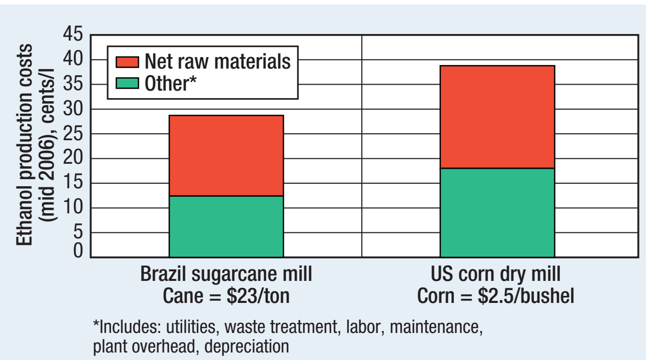

FIG. 4 The ethanol production cost differential of using sugar cane (Brazil) over corn (US).[1]

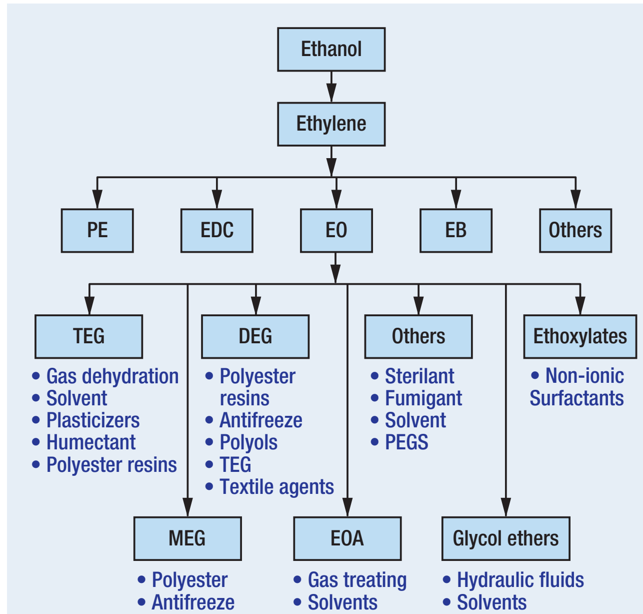

FIG. 6 Chemical/petrochemicals based on ethanol and ethylene.

using ethanol for chemical/petrochemical production. Fig. 3 lists some of the well-known chemicals/petrochemicals that can be produced from ethanol.

Brazil—an ethanol nation. Brazil has a large economic advantage over other areas including the US and Europe. This nation is the lowest-cost producer for ethanol production from sugar cane, which is the main ethanol source in Brazil. Corn is the main ethanol feedstock in the US and Europe. Fig. 4 illustrates the production cost differential when using sugar cane over corn for ethanol production.

Competitive cost structures. From Fig. 4, the cost differential in ethanol production between the US and Brazil is about $0.10/l. Due to the well-developed ethanol production and distribution capabilities of Brazil, this cost differential holds up when compared to other ethanol producers worldwide, as shown in Fig. 5.

Worldwide, based on the well-developed ethanol production infrastructure in Brazil, the Brazilian ethanol-to-ethylene production is the most competitive with petroleum-derived ethylene. Other areas, such as India and China, can also be competitive based upon local situations, such as sugar production capabilities and local government incentives.

Ethanol-to-ethylene processes. Ethylene production is the primary chemical application from ethanol; the ethylene is then used to produce other major downstream ethylene derivatives as listed in Fig. 6.

The ethanol-to-ethylene reaction takes place in the vapor phase, using either fixed-bed or fluidized-bed reactors. For fixed-bed reactors, the reaction is either isothermal or adiabatic. This discussion will focus on the adiabatic, fixed-bed reactor ethanol-to-ethylene process. Fig. 7 is a schematic of an adiabatic fixed-bed ethanol-to-ethylene process.

In this process, ethanol is vaporized and then superheated in a fired heater before being fed to the first in a series of dehydration reactors. The endothermic dehydration reaction requires reheating between reactors to drive the reaction to 99% ethanol conversion or with high selectivity to ethylene. The dehydrator effluent stream is cooled and compressed. After compression, the ethylene stream is washed with caustic, dried and purified in an ethylene column followed by a stripper to reduce carbon monoxide (CO) levels in the final ethylene product.

Fully integrated ethanol-to-ethylene complex. One way to reduce the current pricing disadvantage of ethanol-derived ethylene, as compared to petroleum-derived ethylene, would be to take advantage of the benefits from building a fully-integrated chemical processing unit. The complex would use sugar cane as

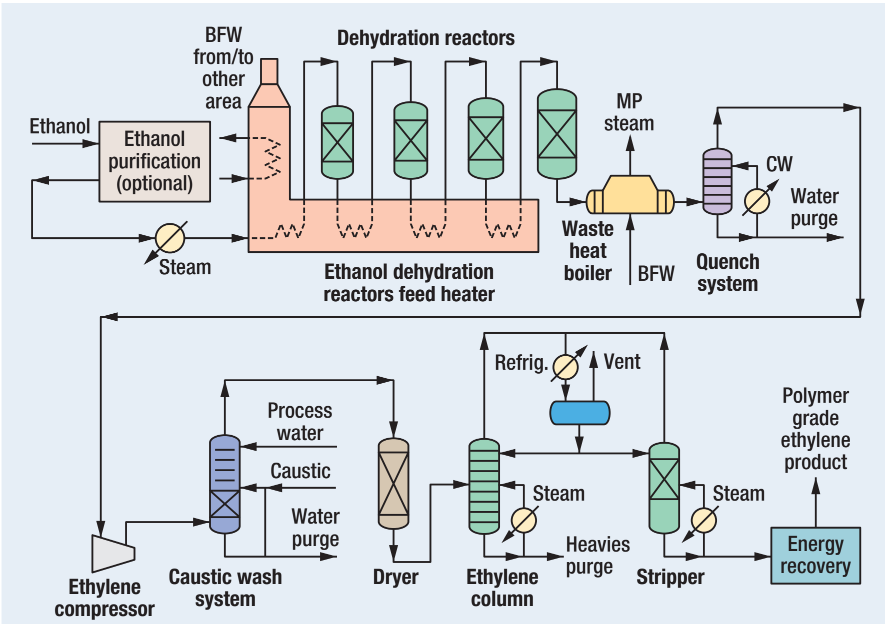

FIG. 7 Flow diagram of polyethylene based ethanol as the feedstock.

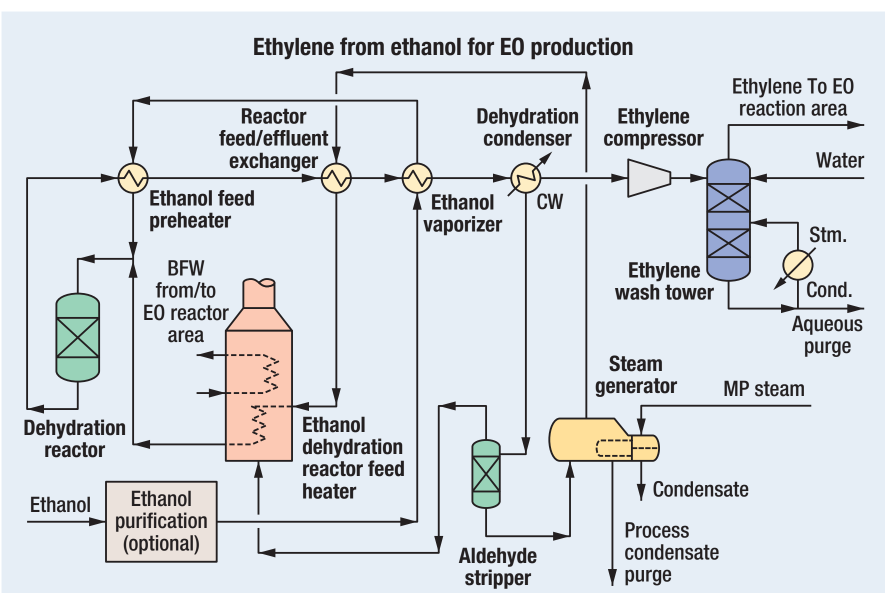

FIG. 8 Flow diagram of EO/EG plant using ethanol as the feedstock.

feed to produce downstream ethylene derivatives such as vinyl chloride monomer (VCM), ethanolamines and high-density polyethylene (HDPE). Such an integrated process was developed in the 1980s for EO/EG production from ethanol as shown in Fig. 8.

When the product ethylene is used to feed an integrated EO or EO/EG plant, the ethanol is vaporized, diluted with steam and fed to a single-bed dehydration reactor. The steam carries sufficient heat to provide endothermic heat of reaction; this yields almost full conversion with a high selectivity to ethylene. The ethylene from the dehydrator is cooled, compressed and washed in preparation for mixing with the EO reactor cycle gas.

The advantages of integrating the ethanol dehydration and EO/EG production process allow using excess steam generated in the process to reduce capital costs associated with ethylene product purification. Such advantages were demonstrated in a commercial plant operating in India since the late 1980s. Table 1 compares the integrated and nonintegrated process. As shown in Table 1, there are both capital and operating cost advantages to integration.

Biorefinery complex. As demonstrated by the production of polyhydroxybutyric acid (PHB), a sugar cane mill producing sugar and ethanol can be integrated with an ethanol-to-EO plant.[5] The dehydration plant will be designed to produce excess ethylene that will be used to produce downstream ethylene derivatives such as VCM or HDPE. The EO produced from the ethanol will be used to produce ethanolamines.

The concept of fully integrating a chemical plant with a sugar mill incorporates key aspects of using readily available renewable sources such as bagasse to produce steam and electricity.

Power/utilities benefits. Producing EO and ethanolamines consumes substantial steam and electricity. However, the sugar mill can be used as the main source to provide energy requirements by using the residue material (mainly bagasse) to generate needed energy and at the same time serving as a means of fulfilling waste-disposal and environmental requirements.[5] It is possible that the wastewater generated from the chemical processes can be sprayed on the sugar cane fields and used as fertilizer.[5] Another advantage of this complex is that the net carbon balance is close to zero since all of the carbon used in the process, both as raw material feedstock and as fuel for energy generation, comes from the sugar cane, and carbon dioxide emitted from the complex is reabsorbed by the sugar cane during its growth.

Case history. The design basis for the complex is to produce 50,000-metric tpy (mtpy), ethanolamines and 60,000 mtpy excess ethylene, that can be used for VCM and/or HDPE. To produce the desired quantity of final products, 90,000 mtpy of ethylene must be processed from the dehydration of ethanol. The 90,000-mtpy ethylene corresponds to 156,500-mtpy ethanol (100%). In a typical sugar mill that is producing both refined sugar and ethanol, about 2 wt% of the raw sugar cane is converted to ethanol. Therefore, to yield 156,500 mtpy of ethanol, over 8 million mtpy of raw sugar cane must be processed.

As stated earlier, the complex can be energy self-sufficient by using residue from the sugar cane (bagasse) to generate the needed energy for the mill and the downstream process units. Typically, about 29% of the sugar cane is left over as bagasse. This material can then be used to generate the electricity and steam necessary for the complex.

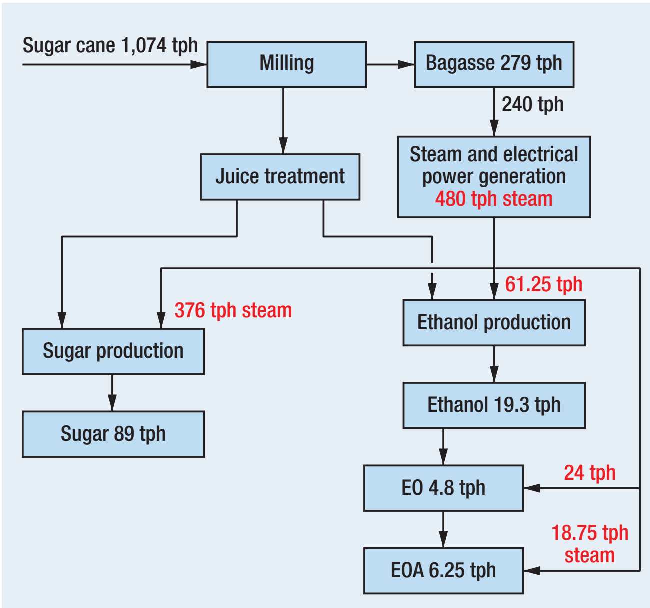

FIG. 9 An integrated biorefinery uses sugar cane to process EO and other downstream derivatives.

Burning bagasse can generate about 2 tons of steam for every ton of bagasse consumed. In the past, the boilers and steam generators were typically run inefficiently to dispose of as much bagasse as possible. The steam requirements for a mill are usually about 550 kg of steam per ton of cane processed.[5] Steam requirements were reduced to about 350 kg of steam per ton of cane by optimizing the mills for heat generation, increasing the use of secondary steam in the juice heaters and vacuum pan, and increasing the number of stages in multiple effect juice evaporators.[5] Optimizations in the ethanol distillation towers also reduced mill steam demand. By improving the overall mill steam requirements, it is now possible to use excess energy generated by the burning of the bagasse to integrate downstream chemical processes such as ethanol-to-EO process.

Fig. 9 is a schematic of the integrated complex, showing how steam generated from the bagasse operates the sugar mill and is integrated into both the ethanol-to-EO and EO-to-ethanolamines processing units.

TABLE 1. Comparison of integrated and non-integrated ethylene production

	Integrated	Non-integrated
Reactor	Single bed	Multi-bed with inter-stage heating
Ethylene purification	Single caustic wash column	Multiple columns and cryogenic distillation
Catalyst performance	99.8% conversion 99.4% selectivity	99% conversion 96% selectivity
Capital cost factor	1	1.5

Future options. As shown in Fig. 9, efficient integration of a sugar cane mill with typical chemical process units can be achieved. Optimizing the efficiency of the mill steam cogeneration unit in which the cane residue (bagasse) is burned can produce sufficient thermal and electrical energy to operate downstream chemical process plants. Along with the energy efficiency benefits provided through integration designs, this concept provides the other benefits including:

- Shared environmental facilities, such as bio-ponds and waste-heat facilities
- Reduced total plot areas due to savings in utility, environmental and other shared offsites
- Lower transportation costs
- Less storage requirements for raw materials and products
- Reduced fuel oil requirement by burning sugar cane waste products—every ton of bagasse used saves about 1.1 bbls of fuel oil
- Lower carbon footprint since carbon source is bio-renewable
- Applies proven technology and does not present any unique processing risks. **HP**

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