Ethanol as a renewable building block for fuels and chemicals

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ABSTRACT

Three factors, i) the ethanol "blend wall", which limits its market as a transportation fuel, ii) advances in production efficiency, and iii) feedstock diversification, could lead to excess ethanol at competitive prices. Those factors have already motivated a search for value-added derivatives (e.g., distillate fuels, olefins, and asymmetric amines). Siting small, low cost, flexible conversion facilities to process ethanol at or near the fermentation plant could encourage the growth of an enterprise. Decreasing the barriers to entry, matching supply and demand, and enhancing access to production incentives are enabling success factors. This review discusses the process

chemistries that might be employed by such ethanol conversion facilities based on market prices. Then, we describe how these technologies might benefit from process intensification to simplify the processing and to avoid large pressures or large temperature gradients typically employed in conventional, large scale facilities.

Introduction

This review summarizes why ethanol should be considered an attractive feedstock for producing renewable chemicals and materials, ranks the candidate products based on market prices, and then proposes technology that could facilitate numbering-up a fleet of distributed facilities to develop the associated enterprise.

Why ethanol? Sustainably sourced ethanol is available today in large quantities at a reasonable price and it can be converted cost-effectively into a slate of products that complement current markets for both specialty and commodity petrochemicals. Global production of ethanol by fermentation is about 29 billion gallons/y.[1] The US produces about half that amount (≈16 billion gallons/year = 47.6 Mt/y) in close to 200 distributed facilities[2], producing ethanol at a total rate of approximately 1 million bbl/day.[3] Its wholesale price in 2019 is less than 0.5 $/kg.[4] Fermentation of the sugars comprising cellulose was formerly viewed as a route to producing very large quantities of ethanol.[5] The cellulosic ethanol industry has not developed with its once envisaged alacrity (it had been projected to supply considerably more than 40 billion gallons per year of ethanol,[5,6] albeit under highly price-sensitive scenarios). Instead, fermentation of syngas[7] and other waste gases (e.g., from steel mills) [8] has now been deployed at scale,[9] providing an environmentally friendly[10] route to additional quantities of the alcohol at a cheaper price.

The major use of ethanol as a transportation fuel is limited by the allowed 10 vol% concentration of ethanol in gasoline (E10). A waiver was granted for the use of E15 in vehicles manufactured in 2007 and later[11] but, E15 is still not widely available in the US.[12] The so-called "blend wall"[13] accounts for the consumption in the US of approximately the domestic production. Higher concentrations would create a larger market but would void the warranties of vehicles and devices (e.g. boats, lawn equipment) not specifically designed to use the more concentrated solutions. Contrarily, the amount of ethanol needed to reach the blend wall will decrease as the average fuel economy of passenger cars increases or as vehicle use decreases, potentially glutting the market.

Which Products? Quantities of ethanol in excess of the blend wall, from any combination of fermentation of plant starches, cellulose-derived sugars, or wastes would be available for producing chemical derivatives, for example those examined in recent reviews of ethanol conversion (Table 1).[14-16] The notional stoichiometries listed in the table are not intended to be representative of any particular process. Rather, they show the sources of the carbon (ethanol or a C_1) and provide a way to coarsely approximate the overall reaction thermodynamics. The reactivity of the hydroxyl group in ethanol permits its ready conversion into industrially significant products and intermediates via dehydration, dehydrogenation, condensation, etherification, and/or oxidation reactions. Products containing three carbons can be prepared from ethanol by hydroformylation, carbonylation or carboxylation of unsaturated products listed in the table. The last column in Table 1 shows the fraction of the global production of ethanol that would be required to satisfy the annual, global demand of each product. It could be expected that diverting ethanol to manufacture the larger volume products would perturb the economics of both the ethanol feed and the products.

Further complicating the identification of the conversions of ethanol that offer compelling economics is the long-observed elasticity[17] in the price of chemical intermediates (solid line in

Figure 1)—those that are produced in largest volume (commodities and fuels) are typically cheaper per unit (say per kg) than those produced in smaller quantities (specialty and fine chemicals). Consequently, revenues across the chemical process industry depend weakly on market volume: the dashed line fit to the revenue data in Figure 1 has a slope of 0.48 (i.e. annual revenue scales approximately with square root of demand for each product considered).

Table 1. Chemical derivatives of ethanol. Global consumption rates and prices from IHS.[18] The consumption rates have units of Mt/y = 10^9 kg/y. Thermodynamics were calculated from values obtained from the NIST Chemistry Webbook[19] using the indicated stoichiometry.

Product	Nominal reaction, $\Delta H^0_{reaction}$/kJ mol^{-1}		Consumption/Mt y^{-1} (year)	Ave Price/USD kg^{-1} (2015-2018)	(Production ÷ C_2H_5OH)/%^{b}
Distillate fuel^a	$5C_2H_5OH + H_2 \rightleftarrows C_{10}H_{22} + 5H_2O$	-350	4540 (2019)	0.59	8500
Ethylene	$C_2H_5OH \rightleftarrows C_2H_4 + H_2O$	43	146 (2016)	0.81	278
BTX^c	$3.6C_2H_5OH \rightleftarrows C_{7.2}H_{8.7} + 3.6\ H_2O + 3_{H2}$	3	120 (2015)	0.90	240
Propene	$C_2H_5OH + CO + 2\ H_2 \rightleftarrows C_3H_6 + 2H_2O$	-165	96 (2015)	1.28	122
Hydrogen	$C_2H_5OH + 3H_2O \rightleftarrows 6H_2 + 2CO_2$	366	85 (2018)	1.99	375
Mixed butenes	$2CH_3CH_2OH \rightleftarrows CH_3C(CH_2)CH_3 + 2H_2O$	-38	43 (2015)	0.86	81
Ethylene glycol	$C_2H_5OH + \frac{1}{2}O_2 \rightleftarrows HOCH_2{-}CH_2OH$	-184	25 (2016)	0.95	32
Isobutene	$2C_2H_5OH \rightleftarrows C_4H_8 + 2H_2O$	-38	14 (2019, est)	1.9	27
Acetone	$2C_2H_5OH + H_2O \rightleftarrows CH_3C(O)CH_3 + CO_2 + 4H_2$	235	6.4 (2016)	1.00	12
Ethylene oxide	$C_2H_5OH + \frac{1}{2}O_2 \rightleftarrows CH_2OCH_2 + H_2O$	-62	26 (2015)	1.34	32
Acetic acid	$C_2H_5OH + O_2 \rightleftarrows CH_3COOH + H_2O$	-443	14.0 (2016)	0.57	12
1,3-butadiene	$2CH_3CH_2OH \rightleftarrows CH_2CHCHCH_2 + 2H_2O + H_2$	89	10.1 (2016)	1.07	20
1-Butanol	$2CH_3CH_2OH \rightleftarrows CH_3CH_2CH_2CH_2OH + H_2O$	-11	5.5 (2014)	3.20	8
Acrylic acid	$C_2H_5OH + CO_2 \rightleftarrows CH_2CHCOOH + H_2O$ $C_3H_6 + 1.5O_2 \rightleftarrows CH_2CHCOOH + H_2O$	43 -637	5.0 (2013)	1.63	4
Ethyl acetate	$2C_2H_5OH + O_2 \rightleftarrows CH_3C(O)OH_5C_2 + 2H_2O$	-465	3.1 (2017)	0.97	4
Acetaldehyde	$C_2H_5OH + \frac{1}{2}O_2 \rightleftarrows CH_3CHO + H_2O$	-181	0.9 (2016)	1.86	1
Ethylene carbonate	$C_2H_5OH + CO_2 + \frac{1}{2}O_2 \rightleftarrows C_2H_4O_2CO + H_2O$	-125	0.2 (2019)	1.50	0.1
Diethyl ether	$2C_2H_5OH \rightleftarrows C_2H_5OH_5C_2 + H_2O$	14	0.04 (2018)	3.30	0.1

a) Fuel prices and market size for distillate (stoichiometry represented as decane) from https://www.eia.gov/petroleum/weekly/archive/2019/190911/includes/analysis_print.php
b) Global production of the product/global production of ethanol
c) Approximate stoichiometry of the world supply of benzene, toluene and xylenes

Of course, revenue does not imply profitability. Each process requires separate techno-economic assessment that considers such factors as carbon yield to finished product, and other operating and capital costs. However, feedstock cost is of paramount importance in any ethanol conversion process. Figure 2 shows a very approximate estimate of the operating cost of producing the products listed in Table 1: the ratio of the market prices of the products divided by the cost of the stoichiometric quantity of ethanol feedstock. Both the prices and the costs will depend on venue, time and other variables. Still, several of the products listed, those significantly above the horizontal line, offer ratios large enough to potentially accommodate processing costs and variability in the price of the products and cost of the reactants. The production of ethylene and distillate, lying near or below the horizontal line, have attracted commercial interest,[20-22] showing that local conditions and/or premia for renewably sourced products may promise incentives beyond those represented by the average prices and cost from which Figure 2 was constructed.

Posada, et al.,[15] present a much more sophisticated analysis, that takes into account economic, environmental and safety considerations and technical risk. In the case of distillate fuel, government subsidies are in place to provide further incentive. Still, the gross simplification depicted in Figure 2 captures the trends they present, with much less effort.

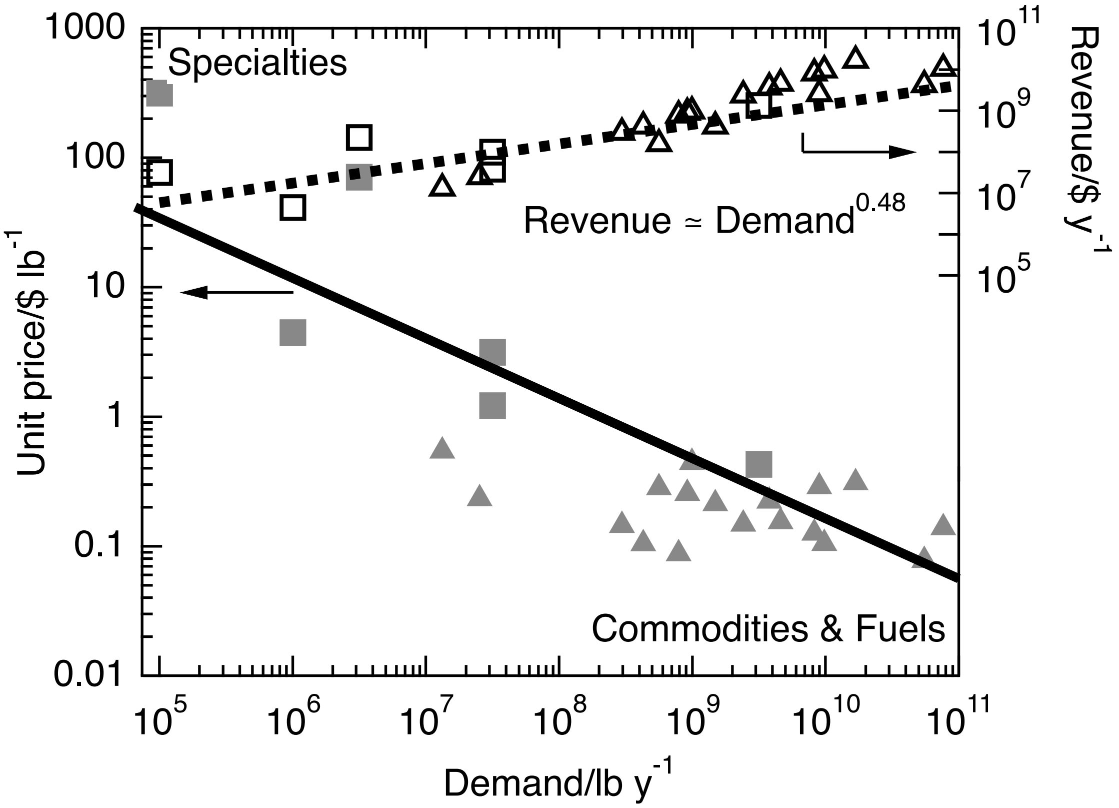

Figure 1. Elasticity of different categories of chemical products. Filled symbols (■, ▲): unit prices; open symbols (□,△): yearly revenue (= unit price × annual demand). Data represented by squares (■, □)were taken from Zamant (Figure 1.1).[17] Data represented by triangles (▲, △) were calculated from the price data and volume data presented in Table 1, scaled to 1989 using the ratio of producer price indices for chemicals[23] in (1989 and 2019) = 112/255.9 and World bank estimates of the ratio of the gross world product in constant 2010 \$ (1989 and projection for 2019) = 36.9 T\$/88.1 T\$.

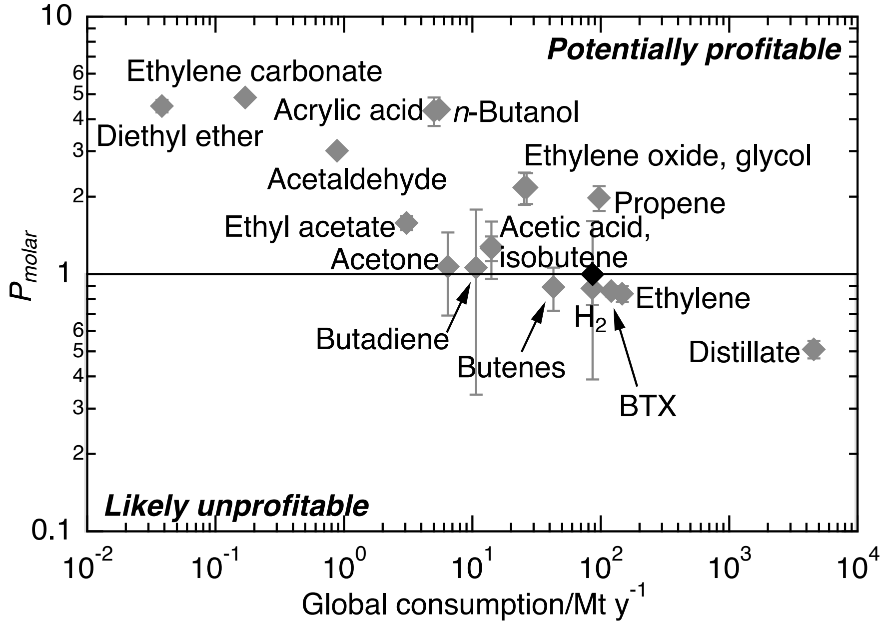

Figure 2 Approximate indicator of operating costs, P_{molar} =ratio of the price of a product divided by the cost of the stoichiometric quantity of ethanol required to produce it. Ethanol (black diamond) lies on the horizontal line that divides the graph into profitable and unprofitable zones, based on the average prices listed in Table 1 (Price of ethanol = 0.027 USD/mol = 1.49 USD/gal). Ranges were estimated from the ranges of prices over 2015-2019.

Discussion

Ethanol is readily available, easily transported long distances, and the chemistry required to implement the conversions summarized in Table 1 is known, at least at bench scale (Figure 3). Still, building an enterprise to use it as feedstock, especially when it yields products for which there is an existing market, is susceptible to each of Porter's Five Forces:[24] actions or threats from suppliers, from buyers, from substitutes, from other new entrants, and, of course, from direct competitors. Some of those competitive forces can be ameliorated by taking advantage of technology that is highly responsive to market fluctuations (rapid turn-up/turn-down) that deploys quickly and frugally, and that encourages favorable supply arrangements by distributing the conversion process to monetize other resources available from the supplier.

In the remainder of this review we summarize the available chemistries and then describe how the processes could benefit from modular process intensification and co-location with the production of ethanol, that is, how process intensification and "scaling out" might serve to accelerate the deployment and improve the competitiveness of each of the conversions listed in Table 1.

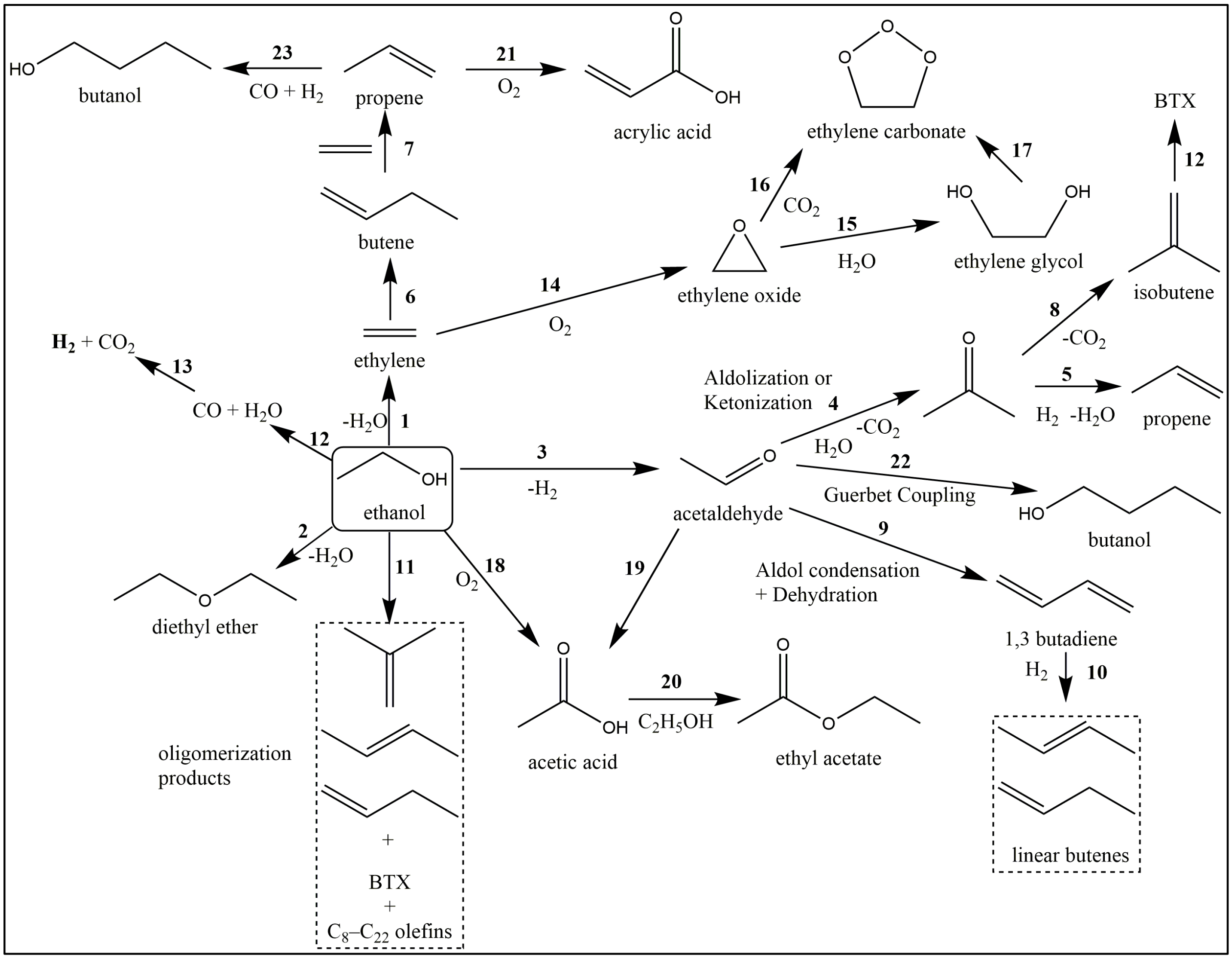

Figure 3. Simplified pathways depicting the conversion of ethanol to the targeted products. BTX: mixture of benzene, toluene, and xylene

Chemical derivatives from ethanol

Ethylene and diethyl ether. Acid-catalyzed dehydration of ethanol vapor can produce both ethylene and diethyl ether (Figure 3 reactions 1 and 2, respectively). The latter is a mildly exothermic reaction ($\Delta H_{reaction}$ = -25 kJ/mol) and thus is favored at low temperature; conversely, ethanol dehydration to ethylene is endothermic ($\Delta H_{reaction}$ = 45 kJ/mol) and is favored at higher temperature (300 – 500 °C). Alumina catalysts[25,26] are most commonly used in industry to produce ethylene and diethyl ether from ethanol but other catalysts, particularly zeolites[27] and supported heteropolyanions, [28,29] can offer higher activity and selectivity (Table 2).

Table 2. Industrial and lab-scale catalysts for ethanol dehydration to ethylene and diethyl ether

Target Product	Catalyst	Reaction Temperature (°C)	Ethanol Conversion (%)	Product Selectivity (%)	Advantages	Drawbacks
Ethylene	Syndol[30] (modified γ-Al_2O_3)	450	99	94	High yield, stable (regen only needed every 6+ months)	High temperature, needs high ethanol concentrations
	Zeolite[27] (H-Mordenite)	180	100	99.9	Near 100% yield at low temperature	Possible stability issues from carbon deposition
	Supported HPA (DTPA/montmorillonite)[28]	250	74	92	High selectivity for reaction temperature	Lower conversion, high cost of catalyst preparation
	HPA ($Ag_3PW_{12}O_{40}$)[29]	220	100	99.2	Near 100% yield at low temperature	Performed in 9% RH air, very sensitive to water content in feed
Diethyl Ether	Commercial γ-Al_2O_3 [31]	250	84.6	85.9	-	Yield
	La/γ-Al_2O_3 [31]	250	76	94	Improved selectivity to DEE	Loss of ethanol conversion

Figure 2 identifies diethyl ether as a potentially profitable product of ethanol. Today, the direct conversion of ethanol into ethylene is not likely to be an economically interesting process by itself, but it may play an intermediate role in the synthesis of several of the more economically promising products (Figure 3) discussed in the following sections. However, we note that Axen's Atol process targets ethylene (in combination with their Futurol technology for cellulosic ethanol production).[32,33]

Acetone. More than 90% of acetone produced worldwide is as a by-product of phenol production from cumene.[34] Acetone can also be produced renewably from ethanol. Ethanol is first dehydrogenated to form acetaldehyde before undergoing either an aldolization or ketonization, with acetone and CO_2 as the respective products. The conversion of ethanol to acetaldehyde (Figure 3 reaction 3) can be facilitated by a dehydrogenation promoter (e.g. Cu, Ag, Pt, etc.) or be base-assisted. Acetaldehyde is then converted to acetone through one of two base-catalyzed condensation routes (Figure 3 reaction 4).[35] The aldolization route between two acetaldehyde molecules produces 3-hydroxybutanol, which is subsequently cleaved through decarbonylation to produce acetone and formic acid that decomposes to CO_2 and H_2.[36,37] Acetaldehyde can also be directly oxidized to form acetic acid before undergoing ketonization to form acetone, H_2O, and CO_2.[37-39] An aqueous feed of ethanol at a water to ethanol molar ratio of 4.5, when passed at 400 C over a CaO/ZnO catalyst yields acetone with 91% theoretical yield (100% conversion of ethanol.[40] At a greater ethanol dilution (water to ethanol molar ratio of 9:1), 96% theoretical yield to acetone at 100% conversion can be achieved over a pyrochlore catalyst, Cu/$La_2Zr_2O_7$, at 400 °C.[41]

Propene. Propene can be produced through ethylene dimerization to butene before undergoing metathesis with excess ethylene, a technology known as the Lummus process (Figure 3 reactions 6 and 7 after dehydration of ethanol in reaction 1). A recent study found that ethylene fed over a heterogeneous system composed of Ni-AlKIT-6 and $ReO_x/\gamma\text{-}Al_2O_3$ at 80 °C and 3 MPa could achieve ethylene conversions of 40% and selectivities of around 45% to propene.[42,43] Propene can also be produced directly from ethanol over catalysts that combine dehydrogenation with an acid/base functionality that promotes condensation reactions. Here, acetone is first formed through ethanol dehydrogenation to acetaldehyde before undergoing either aldolization or ketonization as explained in the preceding reaction mechanisms (Figure 3 reactions 3 and 4). Acetone can then be hydrogenated to form isopropanol before dehydration to propene (Figure 3 reactions 3-5).[44] This chemistry has been previously explored over Sc promoted In_2O_3 catalysts.[45,46]. The production of propene has also recently been demonstrated using a $Zn_xZr_yO_z$ mixed oxide system, previously reported useful for isobutene production (discussed in the following section).[47] Using H_2 as the carrier gas instead of N_2 drives the hydrogenation of intermediate acetone, which shifts the product distribution toward propene instead of isobutene. Nearly complete conversion of ethanol was achieved with a selectivity to propene of 20% (using a 20 wt.% ethanol in water feedstock). This catalyst system permits adjusting the propene/isobutene selectivity.[47] Figure 2 suggests that propene can be a potentially profitable product.

Isobutene. As mentioned above, ethanol can be converted into isobutene directly through a cascade of reactions catalyzed by mixed oxides with acidic and basic sites. Ethanol is first dehydrogenated to acetaldehyde (Figure 3 reaction 3) before undergoing aldolization or ketonization, discussed in the previous section on acetone, in the presence of H_2O to form CO_2 and acetone (Figure 3 reaction 4). Acetone is then converted to isobutene (Figure 3 reaction 8) through aldol condensation to the intermediate mesityl oxide, which then decomposes to form isobutene. Lewis acid-base pairs and Bronsted acid sites can both facilitate these reactions, with the former exhibiting greater activity and stability in the selective conversion of acetone to isobutene.[48] Studies on the catalytic activity of a $Zn_xZr_yO_z$ mixed metal oxide indicate that adjusting the density of Lewis acid-base pairs on the surface can provide both the acidity needed for conversion of acetone to isobutene while limiting the formation of acid-catalyzed dehydration side product ethylene from ethanol.[49,50] This $Zn_xZr_yO_z$ catalyst is able to produce isobutene directly from ethanol at a yield of 60%, nearly 90% of the theoretical maximum yield, with less than 2% activity loss over 200 h time on stream.[51] However, the maximum theoretical carbon yield for isobutene production through this chemistry is only 67% due to stoichiometry. One mole of CO_2 is produced in the conversion of ethanol to acetone regardless of the route, and an additional CO_2 molecule is produced in converting acetone to isobutene (i.e., three moles of ethanol produce one mole of isobutene and two moles of CO_2).

Benzene-toluene-xylene (BTX). Each of these commodity chemicals are currently mainly produced from the fossil fuel industry.[52] Analogous to the oligomerization of methanol to make gasoline-range molecules, catalyzed by controlled pore zeolites, ethanol can be oligomerized to make C_{3+} monomers, mixtures of benzene, toluene and xylene,[53] biogasoline,[54] and distillate fuel[55] (Figure 3 reaction 11). Controlling the acidity of the zeolite helps mitigate catalyst deactivation due to coking.[56] According to Figure 2 there does not appear to be a compelling economic case to make any of those products from ethanol in the absence of mandates or subsidies. However, some companies may still choose to produce such commodities, from bio-based sources, to generate products that can be marketed to consumers as "green". For example, Vertimass[57] is currently commercializing a process for making bio-derived BTX from ethanol and Virent[58] and Anellotech[59] are producing renewably-derived *para*-xylene from sugars and other biomass feedstock. A Ga-ZSM-5 catalyst prepared by an ion-exchange method has demonstrated high yields to BTX from ethanol. At 450 °C, 0.4 h^{-1} $WHSV_{Ethanol}$, and atmospheric pressure, yields of 55% BTX as product are observed, a yield over twice that of oligomerization using H-ZSM-5 (yield of 26% to BTX).[60] Archer Daniels Midland Co and Washington State University also have patented a process for the renewable production of *para*-xylene from acetic acid[61] that, as described in the previous section, can be produced renewably from ethanol through the ethanol to isobutene reaction over $Zn_xZr_yO_z$, after which, BTX can be produced by the sequence of reactions 8 and 12).

Distillates and linear butenes. Conversion of ethanol into distillate fuels has been reviewed recently,[44] so, in this section, we will only briefly summarize challenges with the current technologies and highlight some recent developments. There are several routes that have been demonstrated to produce distillates from ethanol. The first set of pathways involve the dehydration of ethanol to ethylene that is then followed by oligomerization over solid acid catalyst(s) in either one or two processing steps.[62] For single step oligomerization selectivity to undesirable C_1-C_4 light hydrocarbons as high as 40% has been reported. A competition between cracking and oligomerization reactions, extensive coke formation, and the presence of water have been reported as obstacles in producing longer chain products and high catalyst lifetimes.[62] Thus, the control of higher hydrocarbon product formation has been reported to be better facilitated with a two-step oligomerization. For example, Pacific Northwest National Laboratory has developed a two-step oligomerization process that produces primarily iso-paraffin hydrocarbons, forms minimal aromatics, facilitates efficient conversion of high carbon fractions to distillate-range fuels, and minimizes formation of naphtha-like compounds by efficient intermediate product recycling.[62,63] This technology was demonstrated at scale by LanzaTech. Ethanol produced from recycled industrial waste gas was converted to 4000 gallons of jet fuel using the catalytic alcohol to jet synthetic paraffinic kerosene (ATJ-SPK) technology developed at PNNL.[64] A 50 percent blend ratio with conventional jet fuel was used to power a commercial Boeing 747 Virgin Atlantic flight from Orlando to London Gatwick.[65]

PNNL recently reported a new catalytic route for producing *n*-butene directly from ethanol.[66] This route can produce diesel and jet-range blendstock directly from ethanol, which eliminates one unit operation from the current state-of-the-art technology (Figure 3 reactions 3, 9, and 10).[66] This process utilizes a metal-promoted Lewis-acid catalyzed system (e.g., $Ag/ZrO_2/SiO_2$) that has been previously reported for the production of butadiene from ethanol (discussed in the following section).[67] Here, linear butenes are produced instead of butadiene by operating at mild pressures in the presence of H_2, to selectively hydrogenate intermediate butadiene.[66] Oligomerization of the produced butene-rich olefins can subsequently be selectively converted to jet and/or diesel range hydrocarbons.

Ethanol can also be dehydrogenated and then undergo C-C coupling through aldolization reactions before subsequent combinations of hydrogenation, dehydration, and oligomerization reactions to yield various product distillate ranges. One approach, involving aldolization (the ethanol to isobutene reaction, discussed above) results in significant loss of carbon due to CO_2 formation from the ketonization step. That loss reduces the maximum carbon yield to 67% as discussed in the acetone section). Another approach is to perform aldolization through Guerbet coupling (discussed below) before further conversion to distillate products thorugh dehydration and oligomerization. In that case, no ketonization is required and, thus, no carbon is lost as CO_2. However, the approach suffers from low H_2O tolerance, low single pass yields, and the production of oxygenates that decrease the stability of the resulting fuel.[44]

Hydrogen. Steam reforming of ethanol produces synthesis gas that can undergo water-gas-shift to produce a stream that is rich in hydrogen (Figure 3 reactions 12 and 13).[68] The first step is highly endothermic and requires temperatures exceeding 600 K. Precious metals are the most active for this reaction because of their ability to attain high ethanol conversions that lead to improved hydrogen yield. Rh shows higher catalytic activity than other platinum group metals (e.g. Pd, Pt, Ru, etc.).[69] Recently, cobalt-based catalysts at higher metal loadings have emerged as more costeffective alternatives to precious metals, because they are active for C-C bond scission crucial to ethanol steam reforming.[70] Supporting the metal on CeO_2 was found to provide the best combination of ethanol conversion and catalyst stability. Further promotion of Co/CeO_2 catalysts with Zn was found to help suppress unwanted ethanol dehydration and methanation to obtain a C_1 product selectivity to CO_2 of above 90%.[71] Autothermal ethanol reforming in a fluidized bed membrane reactor over a $Pt\text{-}Ni/CeO_2/SiO_2$ catalyst has been shown to have stable performance over 50 h at nearly total ethanol conversion and a hydrogen recovery factor of 67%.[72] While the economics of the production of hydrogen from ethanol do not look compelling (Figure 2), it might be economically viable to use the hydrogen inside the battery limits of a distributed facility.

Ethylene oxide and ethylene glycol. Ethylene oxide is prepared industrially by the partial oxidation of ethylene using supported Ag catalysts at temperatures around 200 - 300 °C (Figure 3 reaction 14).[73] It can also be prepared directly by the partial oxidation from ethanol at high yield using a promoted, supported Au catalyst[74] at temperatures less than 200 °C. Ethylene glycol can then be synthesized through the hydration of ethylene oxide (Figure 3 reaction 15) catalyzed by dilute mineral acids at ~60 °C, or by uncatalyzed hydration at 200 °C.[75]

Ethylene carbonate. Ethylene carbonate is a major component of the electrolyte of lithium ion batteries. It is an aprotic solvent that also is used as a solvent for lubricants, a crosslinking agent in polymer production, in oil field gas washing processes, and as an intermediate in the synthesis of polycarbonate diol.[76] It can be prepared by the direct carboxylation of ethylene oxide (Figure 3 reaction 16)[77,78] or the high pressure (10 MPa) carboxylation[79] of ethylene glycol (Figure 3 reaction 17), made, in turn, from the hydration of ethylene oxide. The use of the high-pressure path avoids inventorying ethylene oxide. Moreover, an ethanol fermentation plant could supply both the ethanol and pure carbon dioxide for this process.

Acetic acid and ethyl acetate. Supported Au catalysts[80,81] are particularly selective towards the oxidation of ethanol to make acetic acid in the liquid phase (Figure 3 reaction 18). Gas-phase conversion has been demonstrated using mixed oxides, e.g., Mo-V-NbO_x/TiO_x, (at yields over 90%),[82] and metal alloys, e.g., CuCr,[83] which dehydrogenate the ethanol to produce acetaldehyde (Figure 3 reaction 3) as an intermediate before further conversion to acetic acid (Figure 3 reaction 19). Subsequently, the acid-catalyzed esterification of acetic acid with ethanol provides a direct path to ethyl acetate (Figure 3 reaction 20), with processes such as catalytic distillation coupled with a membrane separation[84] or a liquid-liquid extraction using an ionic liquid[85] (boiling points of ethyl acetate: 77 °C, ethanol: 78.4 °C, and the water/ethanol/ethyl acetate azeotrope: 78.2 °C). The ester can be synthesized using the Lewis acid-catalyzed Tishchenko reaction[75] from acetaldehyde, synthesized by the dehydrogenation of ethanol[86] or its electrochemical oxidation of ethanol.[87]

1,3-Butadiene. Most butadiene derives from steam cracking of petroleum-derived naphtha, which mostly targets the production of ethylene and propene. However, the increase in shale gas production from hydraulic fracturing over the last decade has made ethylene production from lighter feedstocks, ethane and propane, more economically viable. Those feedstocks yield virtually no butadiene as coproduct so, an alternate route to butadiene could become practicable. Historically, butadiene has either been produced directly from ethanol, known as the one-step or Lebedev process,[88] or produced from co-fed ethanol and acetaldehyde, referred to as the two-step Ostromisslensky process.[89] The two-step process was utilized by Union Carbide and Carbon Chemicals Corporation when butadiene was being produced in the US at an industrial scale during WWII over a TaO_x/SiO_2 catalyst.[90] The generally accepted ethanol-to-butadiene mechanism consists of a cascade of reaction steps that require multifunctional, usually metal-oxide, catalysts to perform the necessary chemical conversions over the surface to selectively form butadiene as a product. Ethanol is first dehydrogenated to form acetaldehyde (Figure 3 reaction 3). Catalysts with dehydrogenation promoters (e.g. Ag, Cu, Pt, etc.) typically facilitate this reaction when the direct conversion of ethanol is employed. Two acetaldehyde molecules then couple through aldol addition to form acetaldol before facile dehydration to crotonaldehyde. This aldol condensation can be base assisted (over catalyst systems containing MgO, ZnO, TaO_x, etc.) or take place over Lewis acids (e.g. ZrO_2, Y, Hf, TiO_2, etc.) on mixed metal oxide ETB catalysts.[91] Crotonaldehyde then undergoes Meerwin-Ponndorf-Verley (MPV) reduction in a six-membered ring transition state with ethanol as the proton donor to form crotyl alcohol and acetaldehyde. Crotyl alcohol is then dehydrated to form 1,3-butadiene (Figure 3 reaction 9). Improving catalyst yield to butadiene by choosing components that limit the formation of the many possible side products in the mechanism has been a chief focus of research, and many catalytic systems (e.g. doped Al_2O_3, promoted $MgO\text{-}SiO_2$, $ZrO_2\text{-}Fe_2O_3$, and zeolite-based catalysts) have been investigated in the literature in the last half-century.[92] We have recently reported[93,94] the development of a $Ag/ZrO_2/SBA\text{-}16$ system that is highly active and stable for the single-step production of butadiene at mild process conditions. At 325 °C, $0.68 h^{-1}$ $WHSV_{EtOH}$, and atmospheric pressure, the catalyst achieves a 67% yield to butadiene that can be maintained over long lifetimes when oxidative regeneration is performed intermittently.

Acrylic acid. While the direct carboxylation of ethylene to make acrylic acid has been the focus of more than 40 years of research,[95-98] selective oxidation of propene (Figure 3 reaction 21) is still the only practicable route to this product.[99] As discussed above, both ethylene and propene can be produced from ethanol, making these routes renewable sources of acrylic acid.

1-Butanol. The current production of 1-butanol relies on an energy-intensive petrochemical pathway of propylene hydroformylation with syngas and propene, which utilizes a rhodium-based homogenous catalyst followed by hydrogenation to produce 1-butanol (oxo-process). From ethanol, 1-butanol can be directly synthesized by Guerbet coupling (Figure 3 reactions 3 and 22)[100] or by hydroformylation of propene generated from ethanol (Figure 3 reaction 23). In the latter case, the carbon monoxide could be produced by reverse water gas shift of carbon dioxide obtained from the ethanol production facility. Among these options, the direct Guerbet coupling pathway is more practical and provides a higher carbon efficiency towards producing 1-butanol.[101,102] The primary barrier for the ethanol based alternative process was due to its difficulty in achieving high product yields (e.g., 1-butanol, 1-hexanol, 2-ethyl-hexanol). A copper-based mixed oxide catalyst was reported to achieve stable, high one pass ethanol conversions with carbon selectivity to higher alcohols >80% (>50% to 1-butanol selectivity) in a fixed bed flow reactor at bench scale. [101,102] The resulting higher alcohols by-product stream can be dehydrated over an acid catalyst to generate α-olefins and be sold as a co-monomer to improve the carbon efficiency and the value of the process.

Process intensification.

The major reason to consider process intensification for the valorization of ethanol is that it should provide a more rapid entrée to markets than a process that followed the trajectory that is conventional in the chemical processing industry.[103] In the context of the conversions summarized above, the four abstract principles of Process Intensification[104] might be interpreted as follows:

Maximize the effectiveness of molecular events: Perform the reactions in the liquid phase to benefit from high concentrations of the condensable reactants and intermediates, while lowering the thermodynamic activity of the products to drive equilibrated reactions towards completion, for example via reaction with separation. The concentration of ethanol in the liquid phase of its azeotrope with water is 16.7 mol/L and 0.0309 mol/L in the gas phase. So, carrying out the reaction in the liquid phase should significantly enhance the rate of collisions of the reactants with the catalysts and with each other.

Accord each molecule the same processing experience: Employ reactors with narrow residence time distributions and promote micro mixing a feature inherent in the use of micro reactors.[105,106]

Optimize driving forces at each scale. Exploit the high rates of transverse transport of energy, mass and momentum afforded by structured packings[107-109] or catalyst-coated walls[110] of microchannel reactors. For the production of ethylene or diethyl ether, good temperature control might be achieved using a microchannel reactor whose reactive walls support a solid acid catalyst.[111]

Maximize synergies among processes. Couple exergonic and endergonic processes, for example pairing the dehydration reactions with oxidation reactions listed in Table 1. In principle the dehydration reaction to form ethylene could be paired with an exothermic reaction, say the production of acetone, running on the opposite side of a microchannel reactor or heat integrated with a separation process.[112] More than half of the conversions considered here are highly exothermic, for example, the partial oxidation of ethylene to make ethylene oxide,[113] oxidation of ethanol to make acetic acid, and the oxidation of propene to make acrylic acid.[114] In those cases, the process selectivity would benefit from rapid removal of the heat, for example through the use of a microchannel reactor. In the case of the endothermic reactions, e.g. steam reforming to make hydrogen,[115-117] the rapid supply of heat is paramount. In the case of ethyl acetate, the electrochemical production of acetic acid[87] inherently has a large dynamic range and is amenable to small scale operation; housing the acid-catalyzed reactions in a microchannel reactor or a microchannel distillation reactor promises to make those operations comparably compact.

Economics of distributed manufacturing and scaling out. Like many enterprises,[118,119] the chemical processing industry benefits from experience,[120] with the learning rate (cost reduction per doubling of experience) depending on the complexity of the process. A learning rate of 20-30%, which is in the range targeted by the US Department of Energy for process intensification,[121] is plausible for a chemical process that involves 8 or more unit operations.[122] We have shown previously[123] that the economics of scaling out (numbering up) and scaling up can intersect for enterprises whose overall throughput is on the order of 1000 t/day. Numbering up is advantageous at smaller throughputs, consonant with the annual production of the more profitable products shown in the right half of Figure 2. The geographic dispersion of the production of ethanol and the inherently faster dynamics of small-scale processes, particularly those that have benefitted from intensification, suggests considerable benefits might accrue in deploying small scale, distributed processes for the manufacture of many of the products discussed here.

Examples

Nearly 120 papers touching on process intensification have been published to date in *Industrial Engineering Chemistry Research*. They include examples of intensification of processes related to those discussed above (Table 3), but none has been implemented for the processes that valorize ethanol discussed here (Figure 3). The lack of examples may stem from the relatively recent advent of modern process intensification combined with the slow pace of advance from laboratory studies for other processes.

Table 3. Examples of Process Intensification related to valorization of ethanol

Reaction or Process	Relevant Products	Mode of intensification	Scale
Ethanol purification[124]	Ethanol feedstock	Divide wall distillation	Production (24 mol/s)
Product separation[125]	Propene, butenes, BTX	Microwick	Pilot (350 mmol/s)
Dehydration[126,127]	Ethylene, dimethyl ether, ethyl acetate, butanol	Membrane reactor	Pilot (15 mmol/s)
Dehydrogenation[128]	Propene, butene	Fluidized bed	Pilot (2.8 mmol/s)
Dehydration with dehydrogenation[129]	Butadiene	Catalytic distillation	Pilot (0.6 mmol/s)
Selective oxidation[130]	Ethylene oxide, acetic acid, acrylic acid	Microchannel reactor	Bench, 2 μmol/s
Isomerization[131]	BTX	Circulating fluidized bed	Pilot (74 mmol/s)
Coupled exo- and endothermic processes[132]	Ethylene oxide	Microchannel reactor	Pilot (28 mmol/s)

We also suggest the use of electrochemistry to partially oxidize ethanol to make acetaldehyde and acetic acid[133] and to make ethyl acetate.[134] These processes could all benefit from the increasing availability of inexpensive and renewable electricity. Electrochemistry should be considered a means of process intensification because it is readily distributable and offers a way to optimize chemical driving forces (the cell potential affects only the charged or polarizable species) of reactions.

Market timing

We can offer no suggestion for when markets for these conversions of ethanol might commence because they will likely depend more on political and societal factors (e.g., formulation and acceptance of climate change regulations) than on technological factors. Once begun, however, we believe it reasonable to assume that they will develop according to an "S"-curve trajectory of consumer products[135] and technologies, as illustrated by the production of ethanol itself (Figure 4). The curve fit to the data in that figure notionally represents a market in which there are many more "imitators" than "innovators" among the customers. Imitators adopt the technology at a rate that depends on the number of previous adopters. Although that model was devised for durable consumer products like refrigerators, it does seem to fit the historical production of ethanol, perhaps owing to a combination of the enterprises who strive to be "first to be second" along with mutual reinforcement of political and business decisions in a market as large as that for a fuel.

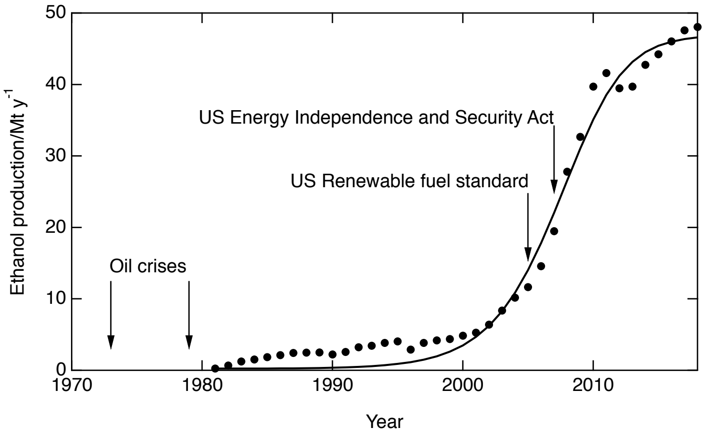

Figure 4. Development of ethanol production in the US. Symbols are annual production rates, compiled by the Energy Information Agency of the US DOE;[136] curve is the functional form suggested by Bass for the introduction of consumer durables.[135]

Conclusion

Ethanol is an attractive feedstock for the production of fuels and chemicals because it is already produced at commercial scale and can be produced from an increasing variety of renewable biomass and waste sources. The price/cost ratio, P_{molar} is typically small (<2) for larger volume products (>10 Mt/y) but P_{molar} is large enough for several moderate volume products (<10 Mt/y) to suggest their economically viable production. Regardless, processes must be employed that are carbon efficient. Further, ordinary market uncertainty coupled with small market volumes suggests consideration of distributed, scaled out facilities, based on intensified processes, for manufacturing those products.

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ABBREVIATIONS

Mt: megaton = 10^9 kg; P_{molar}: ratio of the price of a product divided by the cost of the stoichiometric quantity of ethanol required to produce it.

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For table of contents only