

Advanced alternative fuel pathways: Technology overview and status

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Introduction

Policymakers recognize the significant greenhouse gas (GHG) savings that are possible by transitioning from first-generation, food-based biofuels to alternative, non-food based fuels, i.e., advanced alternative fuels. First-generation biofuels are produced by converting readily available biomass chemicals—sugars, starch or oils—into transportation fuels such as ethanol and fatty acid methyl esters (FAME). Advanced biofuels, on the other hand, are those produced by converting additional chemicals contained in the biomass feedstocks, specifically hemicellulose and cellulose, which are more difficult to extract and convert into transport-grade liquid fuels. For this reason, more complex, advanced conversion techniques are required. Advanced fuels also can include non-biological pathways, such as power-to-liquid or power-to-gas, which are generically referred to as PtX fuels or electrofuels. This paper provides an overview of some of the most promising advanced alternative fuels production pathways.

Figure 1 presents the conversion technology pathways that are assessed

and summarized in this paper. For this figure, as well for all the following figures in this paper that illustrate the individual conversion technology pathways in more detail, yellow boxes indicate processes and green boxes represent an input to the process. Blue boxes represent the desired fuel output, whereas gray boxes are intermediary products. Bold arrows indicate primary steps in the conversion process; narrow arrows indicate less common, or less important, steps. The black, dashed box groups processes that can be applied to the oxygen and hydrogen that is produced in the PtX pathway. PtX refers to electrolysis followed by upgrading.

This paper reviews primary conversion technology pathways, such as electrolysis and gasification, which convert water and biomass, respectively, into gases, as well as cellulosic ethanol conversion. In some cases, such as in the production of cellulosic ethanol, the finished product from the pathways addressed in this paper can be used directly as transportation fuel. In most cases, however, the liquid or gas carrier that is produced from the pathway requires further processing and upgrading, such as

Fischer-Tropsch (FT) synthesis and methanation, before it can be used as a transportation fuel. Hydrothermal liquefaction and fast pyrolysis are other primary conversion technologies that process biomass into crude oils, which are then fed into hydroprocessing or other upgrading technologies to produce drop-in fuel.

This paper synthesizes the best available information on the feedstocks that are or could be suitable for each pathway. Overall, these feedstocks include materials such as lignocellulosic biomass, municipal or industrial waste streams, and waste oils and fats. Lignocellulosic biomass is organic material with a high cellulose and lignin content. It includes agricultural residues such as wheat straw and corn stover, forestry residues, and purpose-grown energy crops such as switchgrass and poplar. In the case of PtX, the feedstocks are electricity and carbon dioxide (CO₂). Also described is any pretreatment, chemical or physical, necessary to prepare the feedstock for the conversion processes.

Although technical assessments for each of these conversion technology

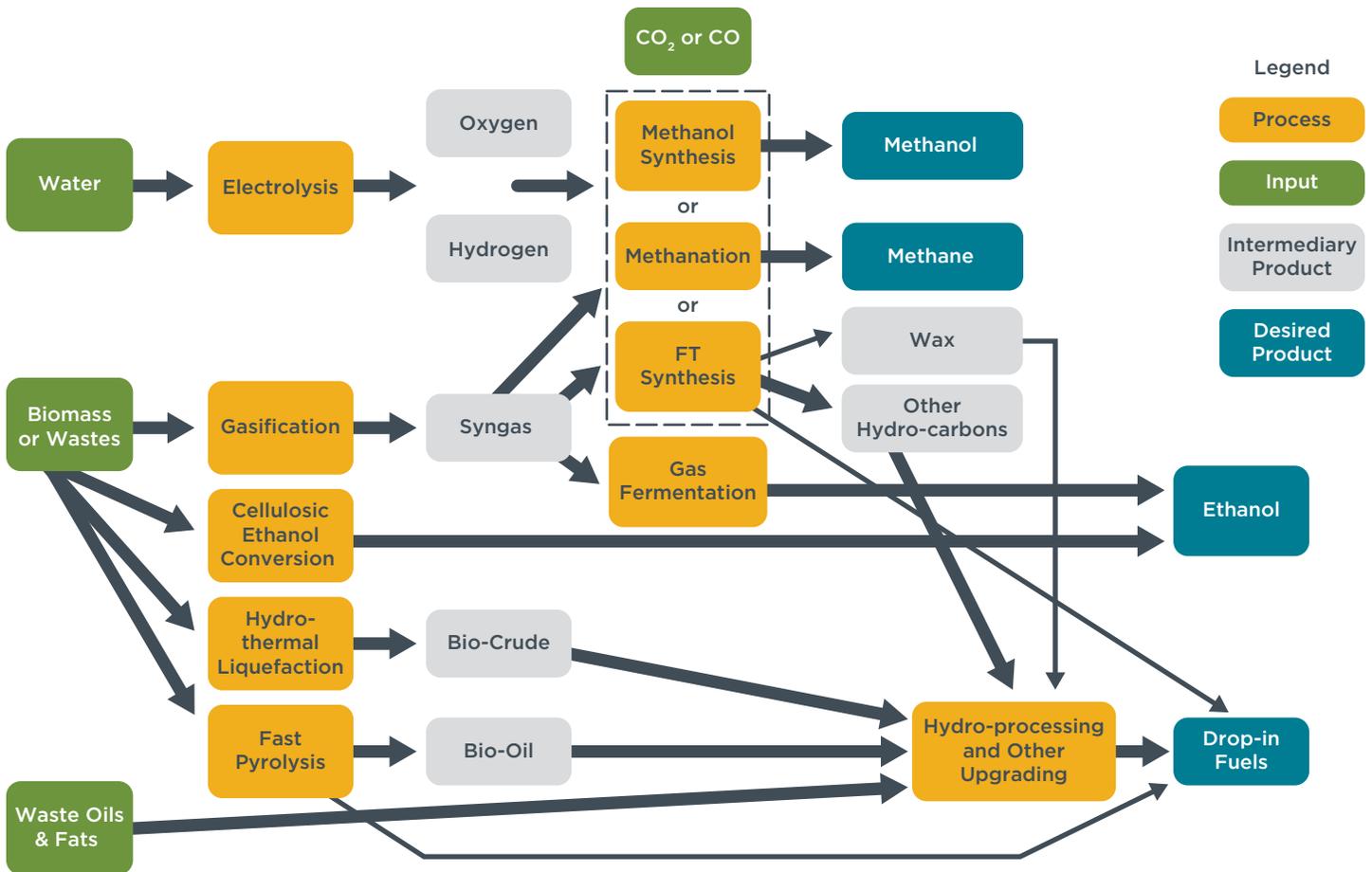


Figure 1: Simplified overview of the conversion pathways reviewed in this paper. Primary steps are highlighted with bold arrows. The black, dashed box groups processes that can be applied to the oxygen and hydrogen that is produced in the PtX pathway.

pathways are available in the literature, there is no study that the authors know of that includes all of these pathways together. This overarching study summarizes how these technologies convert biomass and wastes into fuel and assesses their commercial potential, citing examples, if they exist. It also addresses the major costs associated with these pathways, when information is available. Obstacles that might inhibit commercialization are reviewed for each of the technologies.

Cellulosic Ethanol Conversion

OVERVIEW OF CONVERSION PROCESS

Ethanol is conventionally made primarily from sugars and starches obtained from food crops, such as corn, wheat, sugarcane, and sugar beet. These sugars and starches can be easily converted into ethanol by microbes, such as yeast. Lignin and cellulose, in contrast, consist of long organic

polymer chains that form the physical structure of plants. The process of converting lignocellulosic biomass to ethanol is called cellulosic ethanol conversion. Cellulose is trapped inside the lignin, making it more difficult to convert to ethanol compared to first-generation ethanol production from starches or sugars. Cellulose and hemicellulose are first broken down into monomeric sugars by enzymes, and the sugars are then fermented to ethanol by yeasts. Lignin is a by-product of this process that is typically

combusted on-site for electricity generation, although the use of lignin to extract chemical products with higher added-value is being explored in bio-refinery concepts.

Feedstocks utilized

Within lignocellulosic biomass, the cellulose is bundled into structures, called microfibrils, that are surrounded by lignin and attached to each other by hemicellulose. Typical proportions are 40%–50% cellulose, 25%–30% hemicellulose, and 15%–20% lignin (Menon & Rao, 2012). Cellulose is a polymer of glucose, which means it is made of many glucose molecules bound tightly into chains. Hemicellulose also is a polymer of sugars, but a mixture of sugars, including six-carbon sugars (such as glucose) and five-carbon sugars (such as xylose).

Pretreatment

Pretreatment is the first step in the conversion of lignocellulosic biomass into cellulosic ethanol (see Figure 2). Pretreatment alters the lignin and hemicellulose structures, exposing the cellulose to the action of enzymes and reducing particle size to maximize surface area to mass ratio; this minimizes energy consumption and allows for maximal sugar recovery (Tong, Pullammanappallil, & Teixeira, 2012; Limayem & Ricke, 2012). Further, agricultural and forestry residues often are collected from the ground and therefore contain soil and other unwanted materials that must be removed, usually by washing, so that they do not interfere with the conversion process (U.S. Government Accountability Office, 2016).

There are different feasible pretreatment methods for various kinds of biomass due to differences in physical structure, lignin content, and other considerations (Maurya, Singla, & Negi, 2015). In particular, the pretreatment process for woody biomass differs substantially from that for agricultural biomass (Limayem & Ricke, 2012). Various pretreatment techniques have been developed, each with its own benefits and drawbacks, as addressed in the Obstacles to Commercialization section below. These include the application of physical processes (e.g., particle size reduction through grinding or steam explosion), chemicals (e.g., sulfuric acid), physicochemicals (e.g., liquid hot water combined with ammonium fiber explosion, where high-pressure, liquid ammonia is applied and then the pressure is explosively released), and biological agents (e.g. white-rot or brown-rot fungi and bacteria), or combinations of these (Bensah & Mensah, 2013).

Chemistry of the conversion

Lignocellulosic biomass can be converted into ethanol through either thermochemical or biochemical pathways. In both routes, the recalcitrant structure of lignocellulose is broken down into fragments of lignin, hemicellulose, and cellulose; the hemicellulose and cellulose are then converted into sugars and then ethanol. The thermochemical route, in which the biomass is gasified into syngas—a mixture of gases, primarily hydrogen and carbon monoxide, that also can include carbon dioxide and methane—and then converted into ethanol, is far less common than the biochemical

route, and is described in the sections on Gasification and Gas Fermentation. The biochemical route uses a combination of either enzymes or acids to convert the pretreated cellulosic biomass to ethanol; this pathway includes three steps: hydrolysis, fermentation, and distillation.

Figure 2 illustrates the steps necessary to convert biomass inputs into cellulosic ethanol combustion fuel: pretreatment, hydrolysis, fermentation, distillation and drying, and separation of distillation. Cellulosic ethanol production requires external heat and energy, but in this figure we show only where there is potential for recycling or export of energy. As shown, along with the primary product of ethanol, a secondary, desired product—biogas, which is shown in blue—can also be produced.

Hydrolysis breaks down cellulose into free sugars in order to make the glucose within the cellulose accessible for fermentation (see Figure 2). This process is also called saccharification or cellulolysis. Hemicellulose has more complex sugar polymers as well, but the use of enzymes to cleave these sugar polymers has been found to be cost-prohibitive (Limayem & Ricke, 2012).

Breaking down cellulose through hydrolysis can be done using either sulfuric acid or enzymes. Sulfuric acid can be used in either diluted or concentrated form; concentrated acid hydrolysis is more common and considered to be more practical. One drawback is that undesirable degradation products, such as aldehyde, form during acid hydrolysis.

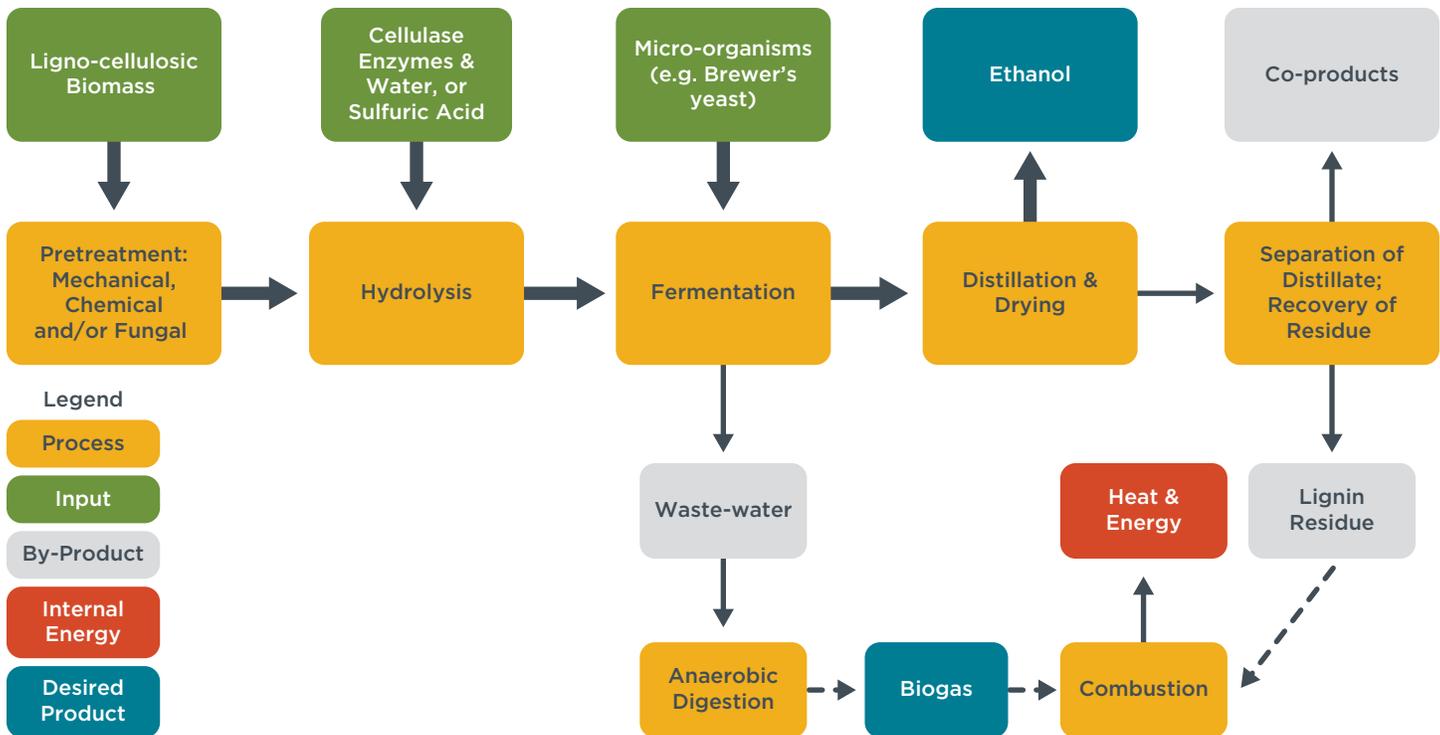


Figure 2: Simplified overview of cellulosic ethanol conversion. Primary steps are highlighted with bold arrows. Dashed arrows indicate optional processes. Adapted from Limayem & Ricke (2012), Baeyens et al. (2015), and Humbird et al. (2011).

In the enzymatic hydrolysis process, cellulases, usually a mixture of several enzymes belonging to three different groups (endoglucanase, exoglucanase or cellobiohydrolase, and β -glucosidase), are used to break down the cellulose. Once the cellulose has been broken down into glucose molecules, the fermentation process uses microorganisms to consume glucose and produce ethanol as an end product (see Figure 2). These microorganisms include brewer's yeast (*Saccharomyces cerevisiae*) and *Escherichia coli*.

The accumulation of the sugar end products in the enzymatic hydrolysis process inhibits the activity of the cellulase enzymes and slows down the reaction. To counter this, in some systems, the hydrolysis and fermentation steps are done together in simultaneous saccharification and fermentation (SSF) processes (Sun & Cheng, 2002). This way the glucose is

consumed as soon as it is produced, allowing cellulolysis to proceed uninhibited. SSF also has the advantage of requiring a single reaction vessel for the two processes, instead of one for each. However, saccharification and fermentation have different optimal temperatures, so for this factor a compromise must be made.

After fermentation, the ethanol is separated from the yeast solids and most of the water by distillation (University of Illinois Extension, 2009). To do this, the broth that comes from fermentation is heated, and ethanol, which evaporates more readily than water, is collected and cooled. However, it is impossible to achieve perfect separation using standard distillation; therefore, the product of distillation, called *hydrous ethanol*, still contains about 5% water.

Hydrous ethanol is sometimes used as a fuel in Brazil (E100), although

in regions where ethanol is used as a blend it is impractical because the water content inhibits blending with gasoline (Volpato Filho, 2008). To remove the remaining water, producers use more energy intensive distillation methods or adsorption columns (Vane, 2008). In an adsorption column, the ethanol is passed across a material called a molecular sieve, which selectively attracts water, leaving dehydrated ethanol. The molecular sieve is then regenerated, which is to say dried, resulting in a cyclic operating scheme.

It is also worth noting that one of the end products of the biochemical conversion of lignocellulosic biomass into ethanol, whether acid or enzymatic, is lignin, which can be combusted and converted to electricity and heat. The economics of cellulosic ethanol production could also be improved were lignin to become a higher-value end product.

COMMERCIAL POTENTIAL

Commercial cellulosic ethanol production generally falls into two categories: smaller, add-ons to existing, first-generation ethanol facilities using starch or sugar crops, or larger, stand-alone projects. Add-on facilities are sometimes called “bolt-on” facilities, primarily using cellulosic waste from the conventional ethanol facility. Bolt-on facilities have generally had more success ramping up production than stand-alone facilities. Quad County Corn Processors is an ethanol plant in Galva, Iowa, with a bolt-on cellulosic ethanol process that uses corn kernel fiber sourced from an adjacent first-generation ethanol facility (Ethanol Producer Magazine, n.d.-b). The Quad County facility’s nameplate capacity is approximately 8 million liters per year of cellulosic ethanol, which is far less than the 130 million-liters-per-year capacity of the adjacent corn ethanol facility (Lane, 2014b). ICM Inc. is operating a pilot bolt-on facility at a conventional ethanol plant in St. Joseph, MO, with a nameplate capacity of nearly 1 million liters per year (Rivers, 2015). The operators claim to have successfully run their unit with corn kernel fiber and switchgrass. Ethanol producer Raízen Energia Participacoes SA, using Iogen Energy cellulosic biofuel technology, has a \$100 million ethanol production plant utilizing sugarcane bagasse located adjacent to a sugarcane mill in São Paulo. In 2016, the plant produced 7 million liters of next-generation ethanol. The facility is slated to produce 40 million liters per year of cellulosic ethanol using sugarcane bagasse and straw (Iogen Corporation, n.d.).

Several large, stand-alone cellulosic ethanol facilities are in development, in early operational phases, and at

least one has been shut down. These facilities use agricultural waste, energy crops, woody biomass, or a combination of all three. POET-DSM Advanced Biofuels operates a cellulosic ethanol plant in Emmetsburg, IA, with a nameplate capacity of approximately 76 million liters per year using corn cobs and corn stover as feedstock (Ethanol Producer Magazine, n.d.-b). Recently, POET filed suit against an engineering company for building an unsatisfactory pretreatment process; in 2010 POET contracted with Andritz, Inc. to build a biomass pretreatment unit, but POET claims that the process never worked at commercial scale, despite one and a half years of redesigns and multiple plant shutdowns (Ellis, 2017; Sapp, 2017). DuPont operated a plant in Nevada, IA, with a nameplate capacity of 114 million liters per year using corn stover until the plant was shut down in late 2017 (Ethanol Producer Magazine, n.d.-b). DuPont cited its merger with Dow as the reason for the decision and is seeking a buyer for the facility (Scott, 2017). POET and DuPont were both operating well below capacity as of April 2016 (Rapier, 2016).

At a smaller scale, several U.S. producers also have developed demonstration projects for cellulosic ethanol conversion at stand-alone facilities. Fiberight planned to convert post-recycling municipal solid waste (MSW) into cellulosic ethanol, but after seven years of research and development, the company decided to instead focus on producing biogas in lieu of cellulosic ethanol. Statements from Fiberight suggest that securing investment for MSW-to-ethanol is very difficult (Lane, 2015b). ZeaChem has a demonstration plant in Boardman, OR, using poplar, straw, and corn stover. The Boardman facility has a nameplate capacity of 946,000 liters per year

(Ethanol Producer Magazine, n.d.-b). Woodland Biofuels has a demonstration plant in Sarnia, Ontario, using woody biomass with a nameplate capacity of 2 million liters per year (Ethanol Producer Magazine, n.d.-a). American Process Inc. Biorefinery has a facility in Thomaston, GA, with a nameplate capacity of approximately 1 million liters per year using sugarcane bagasse and woody biomass (Ethanol Producer Magazine, n.d.-b). The facility also is manufacturing nanocellulose for use as a material in tires and other consumer products (Lane, 2017a). Production of co-products such as these may improve the economic feasibility of cellulosic ethanol production.

In Europe, Beta Renewables operated a plant in Crescentino, Italy, until its closure in late 2017. It has a nameplate capacity of 50 million gallons per year and came online in 2012, but it was never able to reach this capacity. Beta Renewables utilized wheat straw, rice straw, and *Arundo donax* (ETIP Bioenergy, n.d.-a; Schill, 2016). Clariant has a plant in Germany producing ethanol from agricultural wastes (Clariant, 2017). The nameplate capacity of the plant is approximately 1 million liters per year (Clariant, n.d.).

OBSTACLES TO COMMERCIALIZATION

Cost

The conversion process for cellulosic ethanol remains costly. Limayem and Ricke (2012) emphasizes that while technology continues to improve, advanced fuels still require “the most advanced systems analysis and economical techniques designed to cope with feedstock versatility and commodity.” Some research suggests that cellulosic ethanol production may

be cheaper than other production processes using lignocellulosic feedstocks. For example, Peters, Alberici, Passmore, and Malins (2015) estimated the costs for cellulosic ethanol to be lower than for the gasification/Fischer-Tropsch process and hydrotreated pyrolysis oil process, although the authors emphasize that this finding is indicative and not absolute.

Recalcitrance of lignin and hemicellulose

Pretreatment is the most expensive step in cellulosic ethanol production because lignocellulosic biomass is highly recalcitrant, which is to say, hard to break down. Many lignocellulosic feedstocks also are heterogenous and their characteristics can change over time, so it is important for pretreatment methods to be flexible and effective across a range of physical and chemical characteristics (Limayem & Ricke, 2012). However, all of the available pretreatment options have limitations related to cost, effectiveness, or other problems.

Mechanical means of pretreatment can be prohibitively energy intensive. Using heat or chemicals to remove lignin and break down biomass can be effective and is a common method. Chemical pretreatment of lignocellulosic biomass forms the basis of several proprietary cellulosic ethanol production configurations and technologies (Bensah & Mensah, 2013). However, chemical pretreatment tends to produce compounds such as furfural that are toxic and inhibit microbial fermentation. Organic solvents such as ammonia can avoid this problem but are relatively expensive and require solvent recovery systems. Biological pretreatment using white rot or other fungi has low energy requirements

and does not produce inhibitory compounds but requires 4 to 6 weeks and thus incurs costs related to storage space for that time period (Sun & Cheng, 2002).

There is also potentially promising research on genetically modifying plants to reduce the difficulties of processing lignin, either through modifying the lignin's chemical structure or reducing the lignin content. This could be achieved, for example, through down-regulating lignin biosynthesis enzymes in the plant or shifting the plant's energy from lignin biosynthesis to the synthesis of polysaccharides such as sugars and starches (Mood et al., 2013).

High-solids loading

Solids loading refers to the ratio at which solids (i.e., biomass) are added to the system, relative to the water that is needed for the fermentation broth. A higher ratio of solids to liquid translates to reduced water needs, smaller tank sizes, and lower distillation costs. However, increasing solids loading results in decreased sugar yields in the hydrolysis step and decreased ethanol yields in the fermentation step. Kristensen, Felby, & Jørgensen (2009) found that there is a linear, inverse correlation between conversion efficiency and solids concentrations between 5% and 30% initial total solids content by weight (w/w). Ongoing research is attempting to determine the drivers of this relationship with an aim to identifying solutions to increase sugar and ethanol yields. For example, Kristensen et al. (2009) found that hydrolysis products, such as glucose, inhibit the adsorption of cellulase at higher loads. In addition, Jin et al. (2017) found that the presence of ethanol was the major cause of decreased sugar conversion

during SSF, and actively removing it improved the economics of high-solids loading processes.

Cost of enzymes and other chemicals

Both acid and enzyme hydrolysis require expensive materials. Acid hydrolysis requires large quantities of acid, which can be costly to purchase or recycle within the process. For these reasons, research and development has focused mainly on enzymatic hydrolysis for the commercial production of cellulosic ethanol, but cellulase enzymes also can contribute significantly to the ongoing operating cost of a plant (Tong, Pullammanappallil, & Teixeira, 2012). Enzyme costs fall in the range of \$5 to \$20 per kilogram (Johnson, 2016; Liu, Zhang & Bao, 2015).

To minimize enzyme consumption, manufacturers have options such as recycling enzymes for use in subsequent cycles (Lu, Yang, Gregg, Saddler, & Mansfield, 2002). One study reports that this technique can reduce enzyme costs by 50% (Du, Su, Zhang, Qi, & He, 2014). Another solution is to use additives, such as proteins called carbohydrate binding modules (CBMs), that can enhance the enzyme activity (Chundawat et. al., 2011).

C5 sugar content

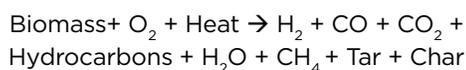
Most yeasts and microbes metabolize glucose and other six-carbon sugars; however, hemicellulose is mostly made of five-carbon (or C5) sugars. C5 sugars, such as xylose and arabinose, are not digested by many organisms; consequently, enzymes that hydrolyze these sugars are less common. Low-cost enzymes that can hydrolyze C5 sugars have not been identified, and thus hemicellulose is currently

cost-prohibitive to process into ethanol. Additionally, research has shown that the presence of some of the C5 sugars, such as xylose, can inhibit the efficacy of cellulase enzymes. These issues are seen with all lignocellulosic feedstocks (Limayem & Ricke, 2012). Research in this area focuses mainly on developing genetically modified microbes that can digest xylose and arabinose (Agbogbo & Coward-Kelly, 2008). Taurus Energy has developed a strain of yeast called XyloFerm that is being tested at the Quad County facility in Iowa (Lane, 2017c). Inbicon also developed a C5 fermentation technology (Ørsted, 2013).

Gasification

OVERVIEW OF CONVERSION PROCESS

Gasification of coal is already widely used as a power generation technology. Increasingly, biomass is also being gasified for power, either alone or co-fed with coal. In the presence of oxygen, but less than what is needed for combustion, gasification converts biomass or organic wastes—for example, the organic fraction of MSW—into syngas. This syngas is a mixture of hydrogen (H₂), carbon monoxide (CO), and CO₂. Simply, gasification is



Tar is the unconverted organic material produced after biomass has been devolatilized during gasification. During devolatilization, tar is released in gaseous form but is condensable at lower temperatures. Char is a high-carbon solid by-product of pyrolysis, gasification, and incomplete combustion of biomass. Syngas can be combusted for electrical power generation.

It also can be used to make liquid and gaseous hydrocarbon fuels, such as diesel, methane, and ethanol.

Feedstocks utilized

Gasification can use a wide variety of feedstocks, including agricultural residues, organic fractions of MSW, forest residues, lignocellulosic energy crops, glycerin, tall oil pitch, and black and brown liquor that are residues of pulp-making. Wood and lignocellulosic residues from forestry and agriculture are the main feedstocks currently used by 80% of the commercial and operating biomass gasification plants (Bermudez & Fidalgo, 2016).

Pretreatment

All feedstocks must be processed into a dry, more uniform material through pretreatment. The objective of pretreatment is to produce input materials for the gasifier with uniform physical properties, high energy density, and low moisture content. Biomass also can be perishable, and some of these pretreatment steps stabilize the biomass so it can be stored or transported more easily. The ideal moisture content for feedstocks for gasification is between 10% and 15% by weight (Bermudez & Fidalgo, 2016). Besides drying, other preprocessing steps may include particle size reduction and compaction of the feedstock; these are dependent on the specific type of gasification technology employed. Research suggests that gasification of solids works better with smaller particle sizes, so, depending on the specific gasification technology, the biomass must be ground, milled, or shredded to an appropriate size (Gaston et al., 2011). At the same time, size reduction takes energy, and there is a trade-off between improved gasification efficiency with smaller

particle size and the additional energy required to achieve that particle size. Some gasifiers require a consistent energy density of the feedstock, while others can tolerate variation. For those that require consistent energy density, torrefaction is another pretreatment option that processes solid biomass at low temperatures (ca. 250°C–300°C) in the absence of oxygen. Torrefied biomass is dry, has higher and more consistent energy density and is easier to grind than untreated biomass, thus behaving similarly to lignite coal (Phanphanich & Mani, 2011).

MSW is inherently heterogeneous, as both household and commercial waste streams contain a variety of waste products including paper products, food waste, and yard trimmings. For a feedstock like MSW, feed handling at a conversion facility must be flexible and able to accommodate a set of heterogeneous feedstocks. Depending on the gasification process selected, the fraction of non-organic components in the MSW such as metal and glass will need to be sorted out and minimized in the feed to the reactor.

Chemistry of the conversion

Figure 3 illustrates the steps necessary to convert biomass inputs into syngas using gasification. Gasification requires external heat and energy, but in this figure we only show where there is potential for recycling or export of energy. After the feedstock has been pretreated, it is gasified and then cleaned; the primary output of this process is syngas, some of which can be combusted on-site for energy.

There are two basic categories of gasifiers: partial oxidation and steam reforming. For partial oxidation gasification, the biomass enters the gasifier along with an oxidizing gas, typically

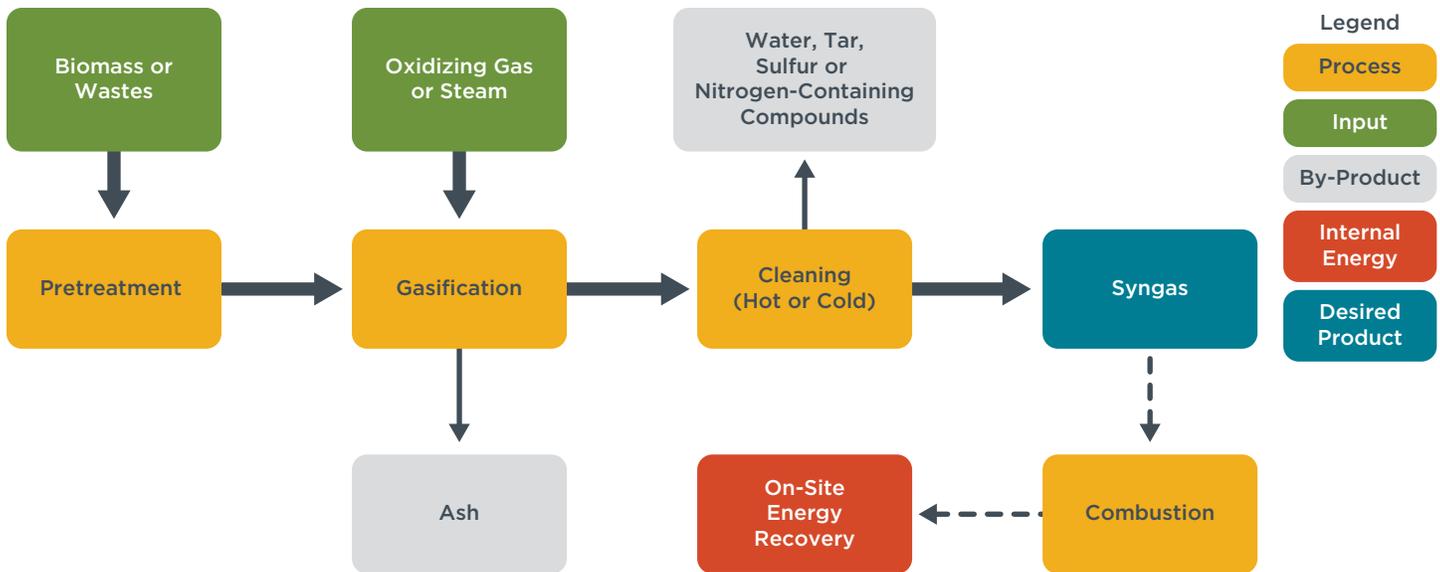


Figure 3: Simplified overview of gasification.

oxygen, air, steam, or a combination thereof. The choice of oxidizing agent depends on the quality required for the syngas and on the operating conditions. The quantity of oxygen introduced is insufficient to combust the biomass. Complete oxidation (i.e., combustion) occurs if there is a perfect match between (a) the ratio of the actual amount of oxygen and carbon from the biomass in the reactor and (b) the stoichiometric ratio between oxygen and carbon that is necessary for complete oxidation. This match is expressed in an equivalence ratio, which divides the first factor by the second. The equivalence ratio is therefore approximately 1 for complete oxidation. Gasification usually is conducted with an equivalence ratio between 0.2 and 0.4 (Bermudez & Fidalgo, 2016). The reaction usually occurs at temperatures between 800 and 1300°C.

In steam reforming, the feedstock enters the gasifier along with steam, and the endothermic energy required for the reaction is provided directly or indirectly through heat exchangers,

which are devices that transfer heat between mediums by conduction.

There is a fundamental trade-off between using oxygen or air as the gasifying agent. Purifying oxygen from air requires additional expense, but air has a very large fraction of nitrogen, an inert gas. Bermudez and Fidalgo (2016) report that for partial oxidation gasification reactions, oxygen gasification is more favorable than air gasification because it allows for smaller downstream equipment and facilitates the removal of CO₂ from the syngas product, which is required for proper synthesis in a Fischer-Tropsch reaction.

Several distinct reactions occur in the gasifier, throughout either steam reforming or partial oxidation (see Figure 3):

- 1. Dehydration:** The high heat of the process evaporates any moisture still present in the feedstock. This steam serves a purpose in subsequent reactions.
- 2. Pyrolysis (also known as devolatilization):** As the biomass continues

to heat up, carbon-containing molecules (i.e., lignin, cellulose, and their decomposition products) break down into gaseous components (i.e., CO₂, oxygenated vapor species) and condensable vapors (i.e., char, primary oxygenated liquids, and water).

- 3. Gasification:** The remaining char reacts with CO₂, water, and oxygen in the presence of heat to form CO, H₂, and methane (CH₄). The volatiles from the previous step may be converted into fuel gases by the secondary reactions of combustion and reforming (Bermudez & Fidalgo, 2016).

The gasifier output is a mixture of hydrogen and carbon monoxide, the two primary energy carriers, along with some combination of water, methane, carbon dioxide, ash, tar, and sulfur- or nitrogen-containing compounds (National Energy Technology Laboratory, n.d.). Ash composition varies depending on the feedstock, but it usually contains some trace elements, such as potassium, calcium, and phosphorus. The ratio of CO and H₂ depends

on the type of substrate and gasification conditions (Du et al., 2016).

A gasification reaction is endothermic, which is to say it requires heat inputs from outside the system, but the process can be designed so that the required energy is provided completely by the recirculation of synthesis gas, the recirculation of tail gas from the Fischer-Tropsch process downstream, or the partial combustion of the solid fuel (Bermudez & Fidalgo, 2016).

Gasification technology

Several different reactor configurations can be used for gasification. The main types are fixed bed, entrained flow, and fluidized bed gasifiers (Bermudez & Fidalgo, 2016). Except for fluidized beds, which are essentially isothermal, there are different zones with varying temperatures and material compositions where the conversion reactions described above take place. The reactor types differ in how and where the feedstock and gasifying agents are introduced and in how ash is handled.

Fixed bed reactors, also called moving bed reactors, follow the same basic configuration as common blast furnaces. Feedstock is introduced at the top and moves down through the vessel through four primary zones: (1) drying, (2) carbonization, (3) gasification, and (4) combustion. Feed is added to the top of the reactor in generally large pieces, i.e., coarse particle size, forming a bed inside the reactor. The oxidizing gas can be added from below the bed (updraft reactor), from the side (cross draft reactor), or from just below the top (downdraft reactor). The oxidation reaction occurs nearest to where the oxidizer is added, with the heat from that reaction powering the others. Downdraft reactors' advantages include their simple design and low tar and particulate formation,

whereas disadvantages include sensitivity to the quality and size of the feedstock; feedstock size limits; low energy efficiency; inability to scale up; and risks of corrosion, explosions, and fuel blockages. Minimizing tar production is important for minimizing impacts on gasifier machinery and for increasing product yield, because tar is essentially unconverted carbon. Updraft reactors' advantages include their simple design; suitability for biomass with high moisture content, low volatility, high ash content, and a variety of particle sizes; low char formation; and high energy efficiency. Disadvantages include risk of explosions, fuel blockages, and corrosion, as well as high tar yield (Bermudez & Fidalgo, 2016).

In fluidized bed reactors, the biomass is either directly injected into the hot fluidized bed or mixed with inert (or sometimes catalytic) bed material such as quartz sand or dolomite, which fosters heat transfer so that there is a uniform temperature in the conversion zone. This gasifier configuration is therefore able to process feedstocks with varying qualities. Contrary to the different zones in the fixed bed reactor, drying, devolatilization, oxidation, and gasification occur simultaneously and homogeneously, producing a synthesis gas with relatively high heating value. These kinds of reactors generally perform better than fixed bed gasifiers. There are two main configurations of fluidized bed reactors: bubbling fluidized beds and circulating fluidized beds.

Bubbling fluidized bed gasifiers are among the most popular for biomass gasification. Their advantages include flexibility regarding feedstock characteristics (e.g., ash content and particle size) and feed rate, and they can be constructed compactly. Disadvantages include potential back-mixing, which limits the conversion efficiency

of solids; complex operation; and a medium amount of tar yield compared to other reactors. Circulating fluidized bed gasifiers are also best for medium-to large-scale gasification processes, are flexible across varying feedstock characteristics, and can be constructed compactly. Compared to bubbling fluidized bed reactors, they have several advantages, such as greater gas-solid contact. Their disadvantages include medium tar yield and complex operation, as well as the potential for damages due to corrosion and attrition (Bermudez & Fidalgo, 2016).

In an entrained flow reactor, very finely dispersed feed is added together with the oxidizing gas. The small particle size allows the reactions to occur much more quickly and allows high conversion efficiency with low tar production. An entrained flow reactor operates at very high temperatures, higher than those in a fluidized bed reactor, causing ash to melt into slag that is then collected from the bottom of the reactor. Of the three primary gasifier configurations, an entrained flow reactor is the most expensive reactor to operate, requiring high amounts of oxidizing gas and high temperatures. It also requires a biomass feedstock that is brittle enough to be broken down to the necessary particle size, such as torrefied biomass. Despite these drawbacks, the clean syngas it produces makes this technology promising for use with biomass (Bermudez & Fidalgo, 2016).

Before the syngas can be used for fuel production, it must be purified and upgraded in order to prepare the proper gaseous mixture for the downstream synthesis. Syngas cleaning can occur via two routes, known as hot and cold (see Figure 3). The cold route is more developed, but the hot route offers better energy efficiency if the syngas will be used downstream at a high temperature. Current research

focuses on how to better implement this route. Cleaning removes tar, sulfur (in the form of H_2S), hydrochloric acid (HCl), ammonia (NH_3), and fly ashes. There are various processes that can be applied downstream of the gasification process to produce usable transportation fuels (Bermudez & Fidalgo, 2016). These include:

- **Methanation:** At temperatures of $700^{\circ}C$ – $1,000^{\circ}C$ and with a nickel catalyst, carbon monoxide and hydrogen are converted to methane and water.
- **Methanol production:** At temperatures of $220^{\circ}C$ – $300^{\circ}C$, a pressure between 50 and 100 bar, and with a catalyst of copper-zinc oxide supported on alumina, methanol synthesis occurs through the reaction of both carbon monoxide and carbon dioxide with hydrogen.
- **Fischer-Tropsch synthesis:** In the presence of a catalyst, the hydrogen and carbon monoxide from syngas are combined into liquid hydrocarbons, the composition of which can be modified according to the desired specifications for the finished fuel, such as renewable diesel. See the Fischer-Tropsch Synthesis section for more information.
- **Gas fermentation:** In the presence of catalysts, syngas can be fed to acetogenic microorganisms, such as *Clostridium ljungdahli*, which then produce ethanol (Limayem & Ricke, 2012). See the Gas Fermentation section for more information.
- **Hydrogen production:** In order to maximize hydrogen production, for example for use in hydrogen fuel cell vehicles, the hydrogen concentration can be increased with a water-gas shift reaction. In the water-gas shift process, steam (H_2O) reacts with carbon monoxide

to produce hydrogen and carbon dioxide. Catalysts are used, typically an iron oxide-based catalyst followed by a copper-based catalyst. Researchers are still working to improve this process.

COMMERCIAL POTENTIAL

Unlike gasification of coal, gasification of biomass and waste feedstocks for transportation fuel production is still in its relatively early stages of development. However, the extensive experience gathered from its application to coal could help the development of the biomass gasification industry. There are major differences between coal and biomass gasification and many of the coal gasifier technologies cannot be directly applied to biomass. For example, entrained flow technology is the most widely used gasifier type for fossil fuel gasification, but entrained flow gasifiers are not available on a commercial scale for biomass. Current research is trying to address the challenge of how to enhance the production of syngas with high H_2 content where impurities such as tar are minimized and capital and operating costs are also reduced (Bermudez & Fidalgo, 2016).

Gasification has higher capital costs than pyrolysis and biochemical processes (Wang & Tao, 2016). Currently, around 75% of commercial biomass gasifiers are fixed bed reactors (Bermudez & Fidalgo, 2016). A study by the International Renewable Energy Agency (IRENA, 2012) found that fixed bed gasifiers have equipment costs that fall between \$1,730 and \$5,074 per kilowatt (kW). Bermudez and Fidalgo (2016) suggest that bubbling fluid bed reactors are a promising technology for biofuels because this reactor type already has been demonstrated across a wide range of conditions. The 2012 IRENA study found that bubbling fluidized bed reactors have

a range of equipment costs that fall between \$2,540 and \$3,860 per kW. For circulating fluidized bed reactors, equipment costs fall between \$1,440 and \$3,000 per kW. Because these cost figures are at least six years old, however, it is possible that in recent years gasification technology has become less expensive.

Fulcrum BioEnergy, which is developing several commercial-scale MSW gasification facilities across the United States, is using steam-reforming bubbling fluid bed reactors (Fulcrum BioEnergy, 2018). In Europe, most existing commercial plants that gasify biomass are dedicated to the production of power or combined heat and power, although there are some pilot projects using gasification for further processing into biofuels for transport (IEA Bioenergy, n.d.). For example, the bioliq project in Karlsruhe, Germany, uses an entrained flow reactor to gasify the bio-crude being produced from fast pyrolysis (bioliq, n.d.-b).

Almost all of the facilities that produce liquid biofuel from biomass gasification at a commercial level are in the United States and Canada. Enerkem, a Montreal, Quebec-based company with a long history of working with bubbling fluidized bed biomass gasifiers, is now converting MSW containing mixed textiles, plastics, fibers, wood and other non-recyclable waste materials into chemical-grade syngas, which is then converted into methanol, ethanol and other chemicals. At its Westbury, Quebec, facility Enerkem processes 17,500 tonnes per year of treated wood (e.g., electric utility poles), wood waste, and MSW into syngas. At its facility in Edmonton, Alberta, Enerkem processes 100,000 tonnes per year of MSW (IEA Bioenergy, n.d.). In the United Kingdom, BioSNG built a commercial facility that will process 10,000 tonnes per year of waste wood and other wastes to produce 22 gigawatt

hours (GWh) per year of grid quality methane through thermal gasification and methanation (Gogreengas, n.d.).

OBSTACLES TO COMMERCIALIZATION

There are several technological issues related to cleaning the syngas so it can be used for downstream conversions. For example, gasification produces tar, which can degrade conversion equipment over time. Tar production can be handled on the front end by pretreating biomass via torrefaction or conducting pyrolysis first (Phanphanich & Mani, 2011). Both of those technologies are under development for use in this application, but neither has been proven cost-effective at a commercial scale. Tar, along with other syngas contaminants, also can be handled on the back end, via syngas cleaning processes. These are proven technologies, used in coal gasification facilities, but they do add additional steps, and thus costs.

Gas Fermentation

OVERVIEW OF CONVERSION PROCESS

Gas fermentation is a hybrid biochemical/thermochemical process where biocatalysts convert gases composed of hydrogen, carbon monoxide, and carbon dioxide into liquid fuels (Griffin & Schultz, 2012). Biocatalysts can be acetogenic microorganisms, such as bacteria in the *Clostridium* genus that use the Wood-Ljungdahl pathway for gas fixation into several fuel products, primarily ethanol, butanol and methanol (Wu & Tu, 2016). Value-added co-products can include a range of chemical products including acetone, isopropanol, 2,3-butanediol, and isoprene (Liew et al., 2016). The bacteria can be genetically modified to

increase product yield and selectivity and produce non-native products.

LanzaTech is the best-known company that has developed and commercialized a gas fermentation process, converting waste gas from industrial processes into fuels, such as ethanol, and chemicals, such as 2,3-butanediol (Wu & Tu, 2016). The waste gases used by LanzaTech include gaseous streams from steel mills that would otherwise be combusted for electricity and process heat or be flared. This technology also reportedly can convert gaseous streams from other industrial processes, such as oil refining and chemical plants, as well as syngas from gasification of forestry and agricultural residues, unsorted unrecyclable municipal waste, natural gas, and coal (Handler, Shonnard, Griffing, Lai, & Palou-Rivera, 2015).

Chemistry of the conversion

Hydrocarbons such as tar inhibit fermentation and adversely affect cell growth; it is thus necessary to clean the syngas first, as described in the previous section on Gasification. After the syngas is cleaned, it is compressed and delivered to the reactor, where fermentation is carried out by microorganisms. The steps necessary for fermenting gas into ethanol combustion fuel are shown in Figure 4. Gas fermentation requires external heat and energy, but in this figure we show only where there is potential for recycling or export of energy. Product recovery comes after fermentation and includes distillation and other techniques. As in the case of cellulosic ethanol conversion, a secondary desired product, biogas (shown in blue), can also be produced by anaerobically digesting waste organic solids.

In the LanzaTech process, carbon monoxide-containing gas is first deoxygenated and then the carbon monoxide is

used as a carbon and energy source by microorganisms suspended in a liquid nutrient solution. If hydrogen is present, it also can be used as an energy source. The microbes secrete fermentation products, such as ethanol, 2,3-butanediol, and acetic acid into the broth. Modifications to the process can change both the nature of the reaction products as well as the ratio between products and co-products. The selectivity and yield of biofuel depend not only on the type of bacteria used, but also on process conditions such as temperature, pH, and syngas composition.

There are also different designs and configurations of bioreactors, and each type has its advantages and disadvantages. The bioreactor design is critical for gas fermentation because it influences the gas-liquid interface and the gas-liquid mass transfer rate (Wu & Tu, 2016). The continuous stirred-tank reactor (CSTR) is a common design: Syngas is continuously injected into the reactor through a diffuser and mechanical agitation breaks the large bubbles into smaller ones. However, CSTR is not economically feasible at a commercial scale because of its high energy cost, so significant research efforts have been undertaken to improve the design of this kind of reactor. Bubble column reactors do not require the same mechanical agitation as CSTRs and they have higher mass transfer rates, but they can have problems with mixing and coalescence. In a trickle-bed reactor, liquid flows down through a packing medium, with the syngas moving either downward (co-current) or upward (counter-current). These reactors also do not require mechanical agitation and have been shown to have higher gas conversion rates as well as higher productivity compared to CSTR and bubble column reactors. Finally, there are hollow fiber membranes (HFMs), where syngas is diffused through micro-size

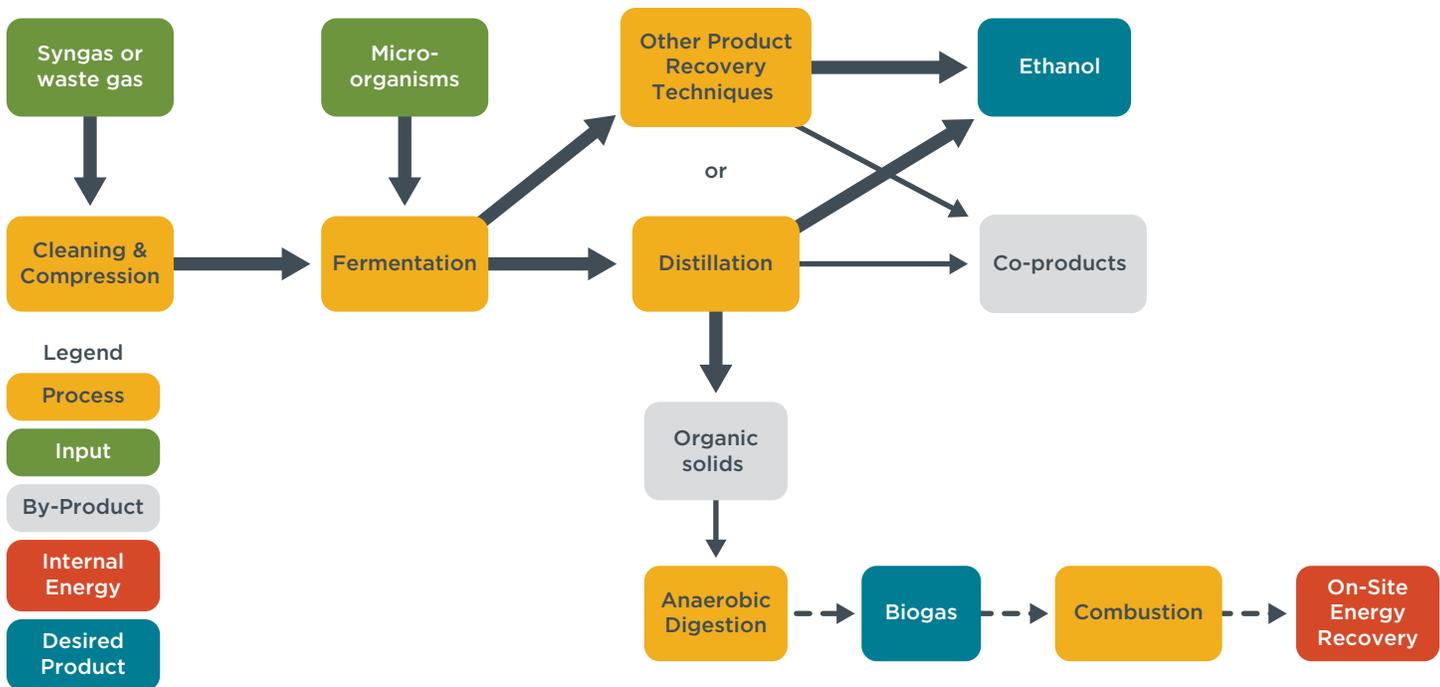


Figure 4: Simplified overview of gas fermentation to ethanol.

pores without forming bubbles. This system offers the highest volumetric mass transfer coefficient, followed by trickle-bed reactors and CSTR (Wu & Tu, 2016).

Wu and Tu (2016) describe several techniques for recovering the desired fuel and other co-products from the fermentation broth, which is the mix of fermentation products. These techniques include:

- **Liquid-liquid extraction:** A dissolved compound is extracted from a liquid mixture using a solvent.
- **Pertraction:** This is a liquid-liquid extraction process in which a membrane is placed between the extracting liquid and the extractant.

- **Adsorption:** Product fuels from gas fermentation, such as butanol, first are adsorbed by certain adsorbent materials, such as resin, and then desorbed, creating a concentrated product.
- **Pervaporation:** In this membrane-based technique, a membrane selectively separates volatile compounds such as ethanol and butanol; these compounds diffuse through the membrane, evaporate, and then are recovered through condensation.
- **Gas stripping:** In this process, an oxygen-free gas, such as nitrogen (N_2), circulates in the fermentation broth in bubbles that then break, inducing vibration of the liquid and the removal of volatile compounds (Ezeji, Karcher, Qureshi, & Blaschek, 2005). It can

operate continuously at an industrial scale, does not harm the fermentation culture, and does not require a membrane, making it one of the most attractive techniques for product recovery (Strods & Mezule, 2017; Wu & Tu, 2016).

Another technique is the LanzaTech conversion process, in which fermentation products are continuously withdrawn from the reactor and sent through a distillation-based separation system for product and co-product recovery (see Figure 4). Waste streams are minimized and recycled internally; for example, organic solids such as spent microbial biomass can be filtered out and digested anaerobically, and with the resulting biogas, can be mixed with some of the vented gas from the reactor for on-site energy recovery (Handler et al., 2015).

COMMERCIAL POTENTIAL

Compared to other technologies, gas fermentation has several advantages: high product selectivity, low reaction temperature, high tolerance to sulfur, and the biocatalyst is much cheaper than the heterogenous catalyst used in the Fischer-Tropsch synthesis process. Gas fermentation also can handle a wider range of H₂:CO ratios in the input syngas than FT synthesis (Wu & Tu, 2016).

To date, the developers exploring this conversion pathway have focused on maintaining stable microbial populations and setting up new reactor technologies. Reactor design still must be optimized to improve pass-through rates, downsize equipment, and integrate energy by using unreacted gases (e.g., unused H₂ from the syngas) for process energy recovery (IRENA, 2016). Further, Wu and Tu (2016) highlight that mass transfer of gas-to-liquid in a bioreactor is the largest rate-limiting parameter, posing a major challenge to gas fermentation.

Researchers also are working on selecting desirable traits in the microbes and blocking out particular metabolic pathways in order to improve primary product yields. Specifically, there are efforts to genetically modify the fermentation bacteria to improve yields, reduce product inhibition, and make them more tolerant to operating conditions that are uninhabitable to other bacteria strains. Capital costs also can be reduced by using new product recovery technologies, such as membranes (IRENA, 2016).

INEOS Bio, Synata Bio, and LanzaTech are the three major companies that have, or have had, precommercial or commercial gas fermentation facilities.

INEOS Bio converts several types of waste biomass including wood waste, vegetative waste, and yard waste into bioethanol (Wu & Tu, 2016). In 2013, INEOS Bio started its first commercial gas fermentation plant in Florida; however, a few years later there were reports that the facility was not producing much fermentation-derived ethanol, primarily due to the sensitivity of the microorganisms to high levels of hydrogen cyanide in the syngas. Recently, INEOS Bio sold this facility, citing changes in the market for ethanol as one of the reasons for this decision (Voegelé, 2016).

As of 2018, the Shougang-LanzaTech Joint Venture is operating LanzaTech's gas fermentation technology at the Shougang Group's Jingtang Steel Mill in Caofeidian, China. This 60 million-liter-per-year facility is converting steel mill waste gas to ethanol. Four further commercial projects are expected to start up in 2019–2020 producing ethanol from refinery and ferroalloy off-gases in India and South Africa; biomass syngas in California; and steel mill off-gases in Belgium. In Japan, SEKISUI has demonstrated ethanol production using LanzaTech's gas fermentation technology on syngas from gasified unsorted unrecyclable MSW that would otherwise be incinerated (Burton, 2017).

OBSTACLES TO COMMERCIALIZATION

Continuous input of the feedstock and removal of the product is necessary to maintain the activity rate of the microorganisms, but this increases the energy necessary for product separation. It is therefore critical to identify methods to either reduce energy demand for product separation, such

as distillation, or instead to genetically engineer or breed strains that are tolerant of more concentrated product. Bacterial activity is also inhibited by acetic acid produced as a by-product, thereby reducing ethanol yield. It is possible that genetically engineering or breeding more selective bacteria strains could mitigate this problem (IRENA, 2016).

Bacterial contamination is another barrier that can have a substantial impact on final yields. To mitigate this, operators must use resilient bacterial strains and reactor systems that are less susceptible to contamination and improve the removal of trace species that can cause population loss (Daniell, Köpke, & Simpson, 2012).

Fischer-Tropsch Synthesis

OVERVIEW OF CONVERSION PROCESS

Fischer-Tropsch (FT) synthesis, illustrated in Figure 5, is used in conjunction with other conversion technologies that produce syngas, such as gasification and power-to-X, which are addressed in other sections of this paper. After the syngas is cleaned, FT synthesis catalytically converts syngas to produce liquid hydrocarbons, which include waxes, drop-in fuel, and other hydrocarbons, as well as tail gas. Tail gas usually is recycled if it is made up mainly of syngas, and it usually is combusted if it is made up mainly of other off-gases. FT synthesis requires energy, but in this figure we show only where there is potential for recycling or export of energy. This product may require further refining before use in the transport sector but in some cases includes fuels that ready to use (see Figure 5).

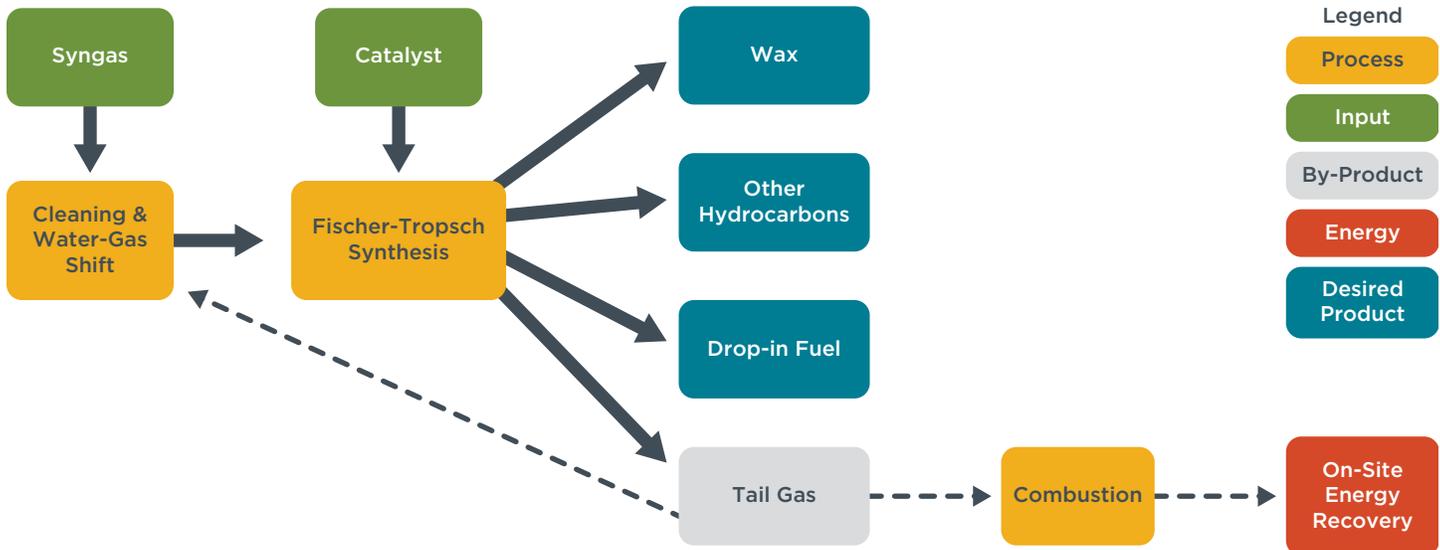
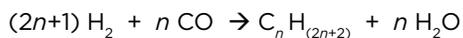


Figure 5: Simplified overview of Fischer-Tropsch synthesis.

Chemistry of the conversion

FT synthesis converts a mixture of hydrogen gas and carbon monoxide into hydrocarbons and water according to the following equation:



The n in this equation indicates that the reaction can be manipulated to produce hydrocarbons with a range of carbon chain lengths. The hydrocarbon distribution is determined by operating conditions, such as temperature, pressure, type of catalyst, etc. Conditions can be chosen to maximize the yield of a particular cut with a higher market value, such as middle distillates (National Energy Technology Laboratory, n.d.).

Prior to the catalytic reaction, the gaseous inputs for the FT synthesis process require cleaning and upgrading. The process is very sensitive to contaminants, especially substances containing sulfur or metals because they can poison the catalysts (Peters et al., 2015). Syngas cleaning is addressed in the Gasification section of this paper. The water-gas shift can

be applied to the syngas to adjust the H_2 :CO ratio if required for FT synthesis. Ideally, the final concentration of inert gases (CO_2 , N_2 , CH_4 , etc.) should make up less than 15% of the gas volume (Bergman et al., 2004).

Fischer-Tropsch synthesis catalysts

Several kinds of metals can be used to catalyze Fischer-Tropsch synthesis: iron, cobalt, nickel, and ruthenium. In practice, ruthenium is prohibitively expensive, and nickel catalyzes some other undesired reactions, so only iron and cobalt are industrially relevant. They have different prices, sensitivities to contaminants, life spans, ideal gas compositions, and ideal operating conditions (National Energy Technology Laboratory, n.d.).

The FT reaction is exothermic, which is to say it releases heat, so an important consideration for the reactors is their capacity to quickly dispel heat from the catalysts to avoid overheating and catalyst deactivation, while at the same time maintaining steady temperature control. Reactors also must facilitate effective mass transfer across

each of the interfaces of solids (catalysts), liquids (hydrocarbons), and gases (carbon monoxide, hydrogen, steam, and hydrocarbons). Finally, because this is a capital-intensive process, reactors must scale up effectively. Three reactor types are considered viable for commercial scale production: multitubular fixed bed reactors, fluidized bed reactors, and three-phase slurry reactors.

Multi-tubular fixed bed reactors are easy to operate and scale up, but they are expensive to construct and have high gas compression costs for the recycled gas feed.¹ They also require long downtimes during replacement of catalysts.

Fluidized bed reactors have higher efficiency in heat exchange and better temperature control. They also require smaller heat exchange area and lower gas compression costs. In addition they are easier to construct than fixed beds. Fluidized bed reactors also allow for online catalyst removal, so there is no downtime for catalyst

¹ Fixed and fluidized bed reactors are described in more detail in the Gasification section.

replacement. They also are more complicated to operate, have erosion problems, and pose some difficulty in separating the fine catalyst particles from the exhaust gas.

Three-phase slurry reactors are a type of fluidized bed reactor wherein the catalyst is suspended in a liquid and the feed gas is bubbled through. They have many of the same advantages as other fluidized bed reactors, including no downtime for catalyst replacement and excellent heat transfer, but it is difficult to separate catalysts and wax (Lappas & Heracleous, 2016).

For small-scale FT systems, monolithic/microstructured reactors are becoming increasingly popular. In a monolithic reactor, there is a thin layer of catalyst on the channel walls, which helps control diffusion of the gas as it flows through the reactor (Holmen, Venvik, Myrstad, Zhu, & Chen, 2013). These reactors are compact, lightweight, and safe, and given their small size, allow for process intensification and capital cost reductions compared to conventional reactors (Arias Pinto, 2016).

Product separation and upgrading

The straight-chain hydrocarbons FT synthesis products include waxes, liquid hydrocarbons, and light gases, which are virtually free of oxygenates, sulfur, metals, and other heteroatoms, which are atoms other than carbon and hydrogen (e.g., oxygen, nitrogen). Generally, when the iron catalyst operates in a high temperature range, usually in fluidized bed reactors, it produces gaseous and gasoline-range products, whereas in the low-temperature range, both iron and cobalt produce more waxy products and straight-run diesel and naphtha (Lappas & Heracleous, 2016). The heaviest hydrocarbon fraction, wax, is usually hydrocracked to break the larger molecules into smaller diesel- or naphtha-sized

molecules, although it also can be sold for its material value for candles and other products (Envia Energy, 2015). Hydrocracking is addressed in the Hydroprocessing section.

The output from an FT reactor is distinct from bio-oil or bio-crude derived from fast pyrolysis or hydrothermal liquefaction, which are addressed in other sections of this paper. FT liquids and waxes are hydrocarbons, containing only hydrogen and carbon. FT synthesis also generates some tail gas, a mixture of the light hydrocarbons that are either generally too small to be sold as fuel, unreacted syngas, or include any inert gases that were contained in the process stream. Depending on the composition of the tail gas, it may be economical to recycle it through the FT reactor or to burn it for power generation.

COMMERCIAL POTENTIAL

FT synthesis is a well-established technology and has been used for decades to produce liquid fuels from coal and natural gas. Sasol and Shell are companies that currently operate commercial scale coal-to-liquid (CTL) or gas-to-liquid (GTL) FT plants (National Energy Technology Laboratory, n.d.). However, gasification of biomass and waste feedstocks is still in its early stages. There are several examples of gasification-FT synthesis facilities using biomass and waste feedstocks in operation around the world, although many are still at the demonstration or pilot scale.

In general, the gasification-FT process is capital intensive compared to other methods for producing cellulosic biofuel (Peters et al., 2015). De Jong et al. (2015) report the minimum fuel selling point to be \$1.50 per liter for FT fuel produced from forestry residues. Liu, Larson, Williams, Kreutz, & Guo (2011) find that FT-derived fuels

usually are less costly to produce when electricity is generated as a major co-product rather than when only liquid fuels are produced. In general, studies on the technology status and economics of FT synthesis suggest that research and development should focus on gasifier designs, syngas quality, product selectivity in chemical synthesis, and process integration and scale (Lappas & Heracleous, 2016).

Choren attempted the world's first commercial gasification-FT plant in 2008 partnering with Shell, Volkswagen, and Daimler using Choren's Carbo-V gasification process and Shell's Middle Distillate Synthesis Fischer-Tropsch process. Due to "uncontrollable costs," insolvency was announced in 2011 and the plant was never completed. There were also several plants in other areas of Europe that failed, such as the Finland Bioenergy Ajos BTL, launched by Vapo Oy and Metsäliitto, and the UPM Stracel BTL in France, both of which had received EU funding in 2010 through NER 300, a large funding program for innovative energy demonstration projects. In both cases, the companies cited uncertainty in the regulatory outlook for advanced fuels beyond 2020 as the reason the projects fell through (Lappas & Heracleous, 2016).

Fulcrum BioEnergy and ThermoChem Recovery International, Inc. (TRI), a gasification technology company, have operated a gasification-FT demo plant in North Carolina converting MSW into jet fuel and diesel. Fulcrum is now developing a commercial scale plant in Reno, NV, that is planned to produce approximately 42 million liters of jet and road fuel from 181,400 tonnes of garbage per year (Tepper, 2017). Fulcrum has agreements with United Airlines, Cathay Pacific, and BP to produce a combined 662 million liters of jet fuel over 10 years. Fulcrum has

seven more plants planned around the United States.

Velocys designs and builds FT reactors for partnerships, rather than running its own plants. Its process uses cobalt catalysts, which Velocys claims offer better yields and stability compared to other catalysts. Velocys operates a pilot plant in Ohio for technology development and participates in two joint projects (Velocys, n.d.). Envia Energy is a joint venture commercial plant in Oklahoma City among Velocys, Waste Management, Ventech, and NRG, using a gasification-FT process at its 17 million-liters-per-year facility, (Envia Energy, n.d.). The plant just came online in 2017 and is not yet up to capacity.

Red Rock Biofuels is another Velocys joint venture that appears to be in an earlier stage of development after receiving a \$70 million grant (Lappas & Heracleous, 2016). The company's stated goal is to make aviation fuel from woody biomass for the military, FedEx Express, and Southwest Airlines. Its plant in Lake County, OR, which was approved for state funding in January 2018, is slated to use 159,000 dry tons of residual woody biomass to produce approximately 61 million liters per year of finished product (Sapp, 2018).

BioTfuel is a joint project among six French partners (IFP Energies Nouvelles, Total, Axens, CEA [a public research organization], Sofiprotéol, and ThyssenKrupp) to convert cellulosic biomass and coal into drop-in diesel through gasification-FT.² This project has a total budget of \$120 million (Lappas & Heracleous, 2016). BioTfuel operates two demonstration plants in Venette and Dunkirk,

France (Total, n.d.). The goal is to open a commercial scale plant by 2020.

The Güssing Renewable Energy demonstration plant in Güssing, Austria, has the world's first functioning fast internally circulating fluidized bed gasification plant, producing syngas that has low nitrogen and a suitable $H_2:CO$ ratio for downstream FT synthesis. Its FT pilot plant, which has been in operation since 2005, produces 5 to 10 kilograms per day of raw product when it is in operation (Lappas & Heracleous, 2016).

OBSTACLES TO COMMERCIALIZATION

Gasification technology

Further research is needed to optimize the choice of gasification technology, for example the reactor type, to be used with FT synthesis in order to meet the stringent syngas quality requirements for FT while minimizing thermal efficiency losses (Lappas & Heracleous, 2016). Most biomass tends to produce a syngas that is relatively low in hydrogen, requiring water-gas shift to increase hydrogen content, which can further increase costs. The barriers to gasification are addressed in more detail in the Gasification section of this paper. Gasification accounts for the bulk (60%–75%) of the capital cost of the combined gasification-FT process (van Steen & Claeys, 2008).

Syngas cleanup

Biomass contains low concentrations of sulfur, which can deactivate the FT catalysts (IRENA, 2016). Sulfur can be removed, but that removal poses another cost trade-off; potential remedies may include cheaper cleanup processes or more resilient catalyst formulations. Low-sulfur feedstocks, such as white woody biomass, could also be used.

Catalyst selectivity

Fischer-Tropsch catalysts have low product selectivity. The FT reaction produces a mixture of hydrocarbons, and although there is some ability to control output, the fraction of desirable fuels is usually less than 40% (IRENA, 2016). The remainder of the output needs to be upgraded through hydrocracking, sold as lower-value product, or burned for electricity. This represents either an added expense or a loss. Possible solutions include improving catalyst technology—for example, through improving catalyst selectivity—or optimizing downstream upgrading processes.

Fast Pyrolysis

OVERVIEW OF CONVERSION PROCESS

In fast pyrolysis, feedstock is heated in the absence of oxygen so that cellulose and other structures break down. This process is related to gasification, which occurs at much higher temperatures with partial oxidation of the biomass and produces mostly gas, and torrefaction, which occurs at much lower temperatures with much lower heating rates and aims at maximizing solid products.

There are three main stages of fast pyrolysis. First, the feedstock is prepared for the conversion process. Second, the conversion process occurs by heating the feedstock in an anoxic environment at very high heating rates. The conversion process generates three products: heavier, condensable gases (tar); off-gases; and a solid char residue (Banks & Bridgwater, 2016). Finally, the tar is condensed to produce bio-oil, which is then processed, refined, or otherwise upgraded to an end product that can be sold as fuel for transport, electricity, or heat,

² A drop-in fuel is made up of hydrocarbons that have no blending limit, such as synthetic gasoline and diesel.

or as a feedstock for chemical production (Bridgwater, 2012).

Feedstocks utilized

Fast pyrolysis can use a wide variety of feedstocks, including cellulosic biomass such as woody material, agricultural residues, and energy crops. The technology also can be applied to industrial waste or by-product materials such as glycerin and black liquor (IRENA, 2016).

Pretreatment

During pretreatment, the feedstock is dried to less than 10% moisture content by weight to reduce the water content in the resulting bio-oil. It also is ground or milled into particles smaller than 5 mm to ensure sufficiently small particles for rapid heat transfer and reaction (Mohan, Pittman, & Steele, 2006). Additionally, washing the feedstock prior to the drying process can reduce the share of unwanted compounds in the bio-oil and ease the

upgrading process later on (Banks & Bridgwater, 2016). Pretreatment is critical to the process because it improves the yields and the quality of the bio-oil. Improving the quality of the feedstock input into the process also reduces the impurities downstream.

Chemistry of the conversion

Fast pyrolysis, which is illustrated step-by-step in Figure 6, is an endothermic reaction requiring temperatures between 475 and 525°C. Following pretreatment, the biomass or waste material is fed into a reactor that yields 40%-70% phase organic compounds (often referred to as pyrolysis oil or bio-oil) and 12%-40% char, water, and gas including light hydrocarbons, carbon monoxide, and carbon dioxide (bioliq, n.d.-a) (see Figure 6). These proportions can vary by adjusting the temperature, feedstock, and reactor residence times. This figure also shows where there is potential for recycling gas for the reactor or exporting energy.

There are several possible reactor configurations. All reactors rely on hot sand or a catalyst to transfer heat to the biomass and to facilitate cracking. Some of the most common reactors are fluidized bed reactors, which are reviewed in the Gasification section. The reaction speed is critical to fast pyrolysis; at slower speeds, less liquid is produced. Consequently, the typical residence time of the feedstock in the reactor is about 1-2 seconds. In order to minimize secondary cracking, which generates increased quantities of undesired products like water, off-gas, and tar, the char by-product must be removed and vapors must be cooled quickly (Banks & Bridgwater, 2016).

Depending on the reactor type, the off-gases, which generally consist of light hydrocarbons such as methane and ethane, as well as carbon dioxide and carbon monoxide, are burned to supply heat or power for the process. In some cases, the gas could also be used as the fluidizing vector in a

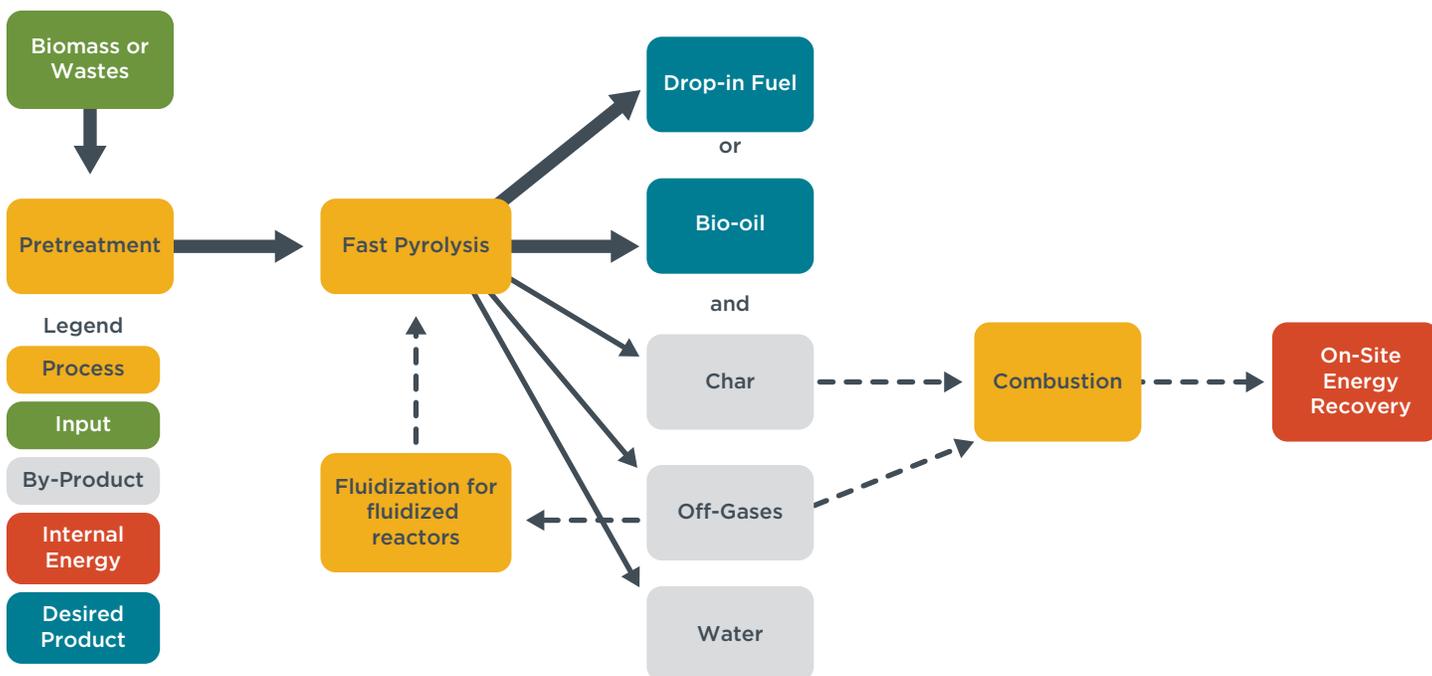


Figure 6: Simplified overview of fast pyrolysis.

fluidized bed, thereby increasing the $H_2:CO$ ratio and therefore the hydrocarbon content in the bio-oil. In some processes, the char produced in the pyrolysis reactor is burned to reheat the sand or catalyst to provide heat for the pyrolysis reaction. In other cases, it is combined with the oil.

The primary product of the pyrolysis pathway, the bio-oil, generally has an oxygen content between 15 and 40% (Czernik & Bridgwater, 2004). Its composition depends on a variety of factors, including feedstock material composition, pyrolysis temperature, residence time in the reactor, heating rate, collection system, and storage conditions. The bio-oil is composed of hydrocarbons, water, and a small amount of ash. The bio-oil retains between 50 and 70% of the energy of the input biomass feedstock. The remaining energy is contained in the char and off-gases (Banks & Bridgwater, 2016). The energy density of the bio-oil is 50% that of petroleum due to the bio-oil's relatively high oxygen content (Czernik & Bridgwater, 2004). Oxygen content increases the corrosivity of the bio-oil as a fuel. In addition, many of the oxygen-containing molecules in bio-oil are very reactive compounds that react with each other, making the mixture unstable and susceptible to degradation over time. Bio-oil is therefore impractical to store and challenging to process downstream (IRENA, 2016).

The high oxygen content in bio-oil also means that greater quantities of water can be mixed in the oil compared to conventional petroleum. Dissolved water further decreases the energy content of the bio-oil and makes further processing of the oil more

difficult. A certain amount of organic material dissolves in the water, consisting mostly of light acids, such as acetic acid. These organic compounds in the water phase are essentially "lost" product. Technology developments to collect and upgrade these compounds would improve the efficiency of the fast pyrolysis process. BTG Empyro is researching recovery of light acids, although it is unclear whether that is for improved fuel yields or to sell as co-products. Despite these drawbacks, water contamination has the advantage of making the oil less viscous so that it flows more easily (Czernik & Bridgwater, 2004).

The physical and chemical properties of the bio-oil make it unusable except in lower-value uses such as stationary combustion, for example, stationary heat and steam generation. For the liquid to be used in the transport sector, it needs further upgrading to remove oxygen, water, ash, and other contaminants, and to reduce its viscosity. There are a number of upgrading technologies that can be used and are being tested. Simple physical processes such as filtration and adding solvents can remove solids and ash and reduce viscosity, respectively (Bridgwater, 2012).

An alternative to conventional fast pyrolysis is *catalytic pyrolysis*, which produces a better quality bio-oil that requires less upgrading (Banks & Bridgwater, 2016). Several kinds of catalysts can be used, depending on the desired product; naturally-occurring catalysts such as dolomite are the cheapest. There are several reported advantages of catalytic upgrading compared to other conversion processes. This process has been shown to control product distribution

and selectivity (i.e., narrowing the molecular weight range of the liquid products so that they are consistent with fossil fuels) to a better extent than other processes. In some cases, the vapor output from the process can be directly upgraded to drop-in liquid fuel; hydroprocessing is thus unnecessary. If hydroprocessing is used for upgrading bio-oil produced from catalytic pyrolysis, less light off-gases are produced compared to conventional bio-oil because of the lower oxygen content of the catalytic pyrolysis bio-oil. Catalytic pyrolysis requires potentially simpler pretreatment processes. Lastly, the reaction temperature can be lower than non-catalytic fast pyrolysis, thereby reducing energy consumption and cost (Thilakaratne, 2016).

One commonly discussed option is to co-process bio-oil with petroleum oils in refineries. Bio-oil could be co-processed in fluid catalytic cracking (FCC) units together with the heavier fractions of fossil crude; many refineries in the United States and Europe are equipped with this equipment (California Air Resources Board, 2017). For example, the CRI Catalyst Company, owned by Shell, has a license to scale up the new catalytic thermochemical process IH². Hydrotreatment also can be applied to bio-oil co-fed with petroleum oils in refineries; this is further covered in the Hydroprocessing section. At the same time, the oxygen content of bio-oil may need to be reduced before it can be processed in petroleum refineries (IRENA, 2016).

COMMERCIAL POTENTIAL

Since the fast pyrolysis technology emerged in the 1980s, much of the

focus has been on scaling up reactor technologies, reducing product moisture content, improving bio-oil oxidative stability, and decreasing the amount of solids produced. IRENA (2016) found that some of the greatest opportunities for improving this technology involve introducing catalysts that promote higher selectivity of desirable alkanes in the bio-oil and thereby improve yields.

There are no commercial examples of bio-oil from pyrolysis or upgraded bio-oil being used as a transport fuel. A 2015 study estimated that commercial hydrotreated bio-oil would cost \$1,758 per tonne, far higher than the current price of petroleum (Peters et al., 2015).³ However, the study also found that producers reduced hydrotreated bio-oil conversion costs threefold between 2009 and 2014; therefore, it is possible this downward trend could continue. Most of these cost reductions have come from reducing the cost of upgrading the bio-oil to a transport fuel. Famously, the company KiOR performed pyrolysis using wood as a feedstock at its facility in Columbus, MS. KiOR, recently renamed Inaeris, filed for bankruptcy in 2014 after a scandal emerged in which the company had misrepresented the technology and production costs to shareholders (Lane, 2016).

Many existing facilities generate bio-oil for stationary combustion only. IEA Bioenergy maintains a global database of biomass conversion facilities, and as of January 2018, it contained 27

operational fast pyrolysis facilities, primarily in the United States, Canada, and the EU (Germany, the Netherlands, Sweden, and Finland). Four more facilities are under construction in Canada, and one more in Germany. There are three facilities in the United States and one in Finland that are non-operational. Companies with multiple operating facilities include BTG (Netherlands), Ensyn (Brazil and Canada), Fortum (Finland), Karlsruhe Institute of Technology (Germany), and Red Arrow (United States) (IEA Bioenergy, 2018).

BTG BioLiquid, part of the BTG Biomass Technology Group, specializes in optimizing pyrolysis technology. The company's first-of-a-kind commercial plant in Hengelo, Netherlands, has been designed to process 40,000 tonnes of biomass per year, and the company believes that the success of this plant bodes well for full-scale fast pyrolysis technology commercialization (Banks & Bridgwater, 2016).⁴ BTG BioLiquid also opened a pilot plant in Enschede, Netherlands, in 2015 that generates heat, electricity, and bio-oil, which is intended for boiler and furnace applications.

Ensyn is known to have some of the most competitive costs of production in the industry, with reported capital costs in the range of \$1.32-\$1.59 per liter and production costs around \$0.33 per liter for a prototypical 76 million-liter-per-year plant (Lane, 2015a). As of 2017, Ensyn, Arbec Forest Products, Groupe Rémabec, and Honeywell UOP were constructing a first-of-a-kind

commercial pyrolysis plant in Quebec that is slated to produce almost 40 million liters per year from a mix of forest residues. Some of the bio-oil produced will be used for heating, and some will be used for refining into transportation fuels, although the split has not been shared publicly (Ensyn, 2016). The joint venture claims it can use existing oil refining technology, which would represent a major development in making pyrolysis a practical technology for transportation fuel production.

In 2013, a consortium of VTT of Finland, Metso (now Valmet), UPM, and Fortum built a commercial plant with a capacity of 50,000 tonnes per year of bio-oil that is integrated into Fortum's combined heat and power plant in Joensuu, Finland. The plant uses forest residue, wood chips, and sawdust (Perkins, 2018). The primary focus has been on thermal pyrolysis but various catalysts also have been tested.

The bioliq pilot plant at the Karlsruhe Institute of Technology in Germany can process up to 500 kilogram per hour of biomass, although it is not run at full capacity (bioliq, n.d.-a). Bioliq sends its bio-oil and char to a gasifier to make syngas, which is then used to make transportation fuels.

OBSTACLES TO COMMERCIALIZATION

There are some obstacles relating to the feedstock and pretreatment process. Grinding, milling, and drying the feedstock represent a substantial cost. In addition, particle shape and size distribution affect processing.

IRENA (2016) reports that low yields are one of the greatest technology barriers to commercialization of

³ Calculated from 1,647 € per tonne using the average exchange rate in 2015 of 0.937 EUR/USD from the U.S. Internal Revenue Service (<https://www.irs.gov/individuals/international-taxpayers/yearly-average-currency-exchange-rates>).

⁴ Based on the original statistic that this plant can produce 5 tonnes per hour and assuming 90% uptime, i.e., that the plant runs for 8000 hours per year.

fast pyrolysis. Pyrolysis is an endothermic reaction, and ensuring sufficient heat transfer into the system can be a substantial economic barrier, as systems for external heat transfer can add substantially to the overall cost of the process (IRENA, 2016). The Bioeconomy Institute at Iowa State University claims that autothermal pyrolysis improves the pyrolysis process because the energy demand of the endothermic reaction is balanced with the energy released from exothermic reactions; this is common in gasification and steam reforming. Autothermal pyrolysis eliminates the need for heat exchange and ancillary equipment and results in a higher feedstock throughput that does not degrade product yield or quality (IRENA, 2016).

Additionally, it is challenging and expensive to upgrade bio-oil. For example, the high water content of bio-oil is harmful to hydrotreating catalysts. Because bio-oil is very corrosive, it requires that refineries use metal equipment resistant to corrosion, usually stainless steel. This is more expensive than the carbon steel generally used in petroleum refining. In order for this bio-oil to be co-fed into conventional refinery units, which would bring significant cost savings, it has been reported that the high oxygen content would first need to be reduced (IRENA, 2016). Catalysts also can rapidly deactivate due to oxygen content (Banks & Bridgwater, 2016). More robust and selective catalysts need further development, and the cost of this process needs to be reduced for it to be commercially applied (Du et al., 2016).

Hydrothermal Liquefaction

OVERVIEW OF CONVERSION PROCESS

Hydrothermal liquefaction (HTL), also known as hydrothermal upgrading, is a process that converts high-water content biomass, or biomass slurries, into liquid fuel, as illustrated in Figure 7. Following pretreatment, the biomass slurry is heated and pressurized to convert it to bio-crude. Bio-crude is an intermediary product that has a higher energy density than the original form of the biomass, making it easier to transport to a facility where it can be hydroprocessed in a manner similar to conventional crude to produce drop-in fuels (IRENA, 2016). The HTL process also generates aqueous phase (i.e., carbon oxygenates and other organic materials suspended in water), solid residue (mainly char), and gaseous by-products (primarily carbon dioxide and carbon monoxide) (see Figure 7). The aqueous phase can be recycled, reducing requirements for fresh water and potentially enhancing the total yield. This process water also can be treated anaerobically to produce biogas (shown in blue) or via catalytic hydrothermal gasification to produce syngas (also in blue), although anaerobic digestion of process water has not been demonstrated experimentally (Biller & Ross, 2016).

Feedstocks utilized

A variety of feedstocks can be processed through HTL, including MSW, algae, manure, distillers' grains with solubles (DGS), and food wastes. HTL is particularly desirable for converting feedstocks with high water content because the process does not require an additional pretreatment drying

step, as with other thermochemical processes described above.

Pretreatment

The feedstock for HTL usually contains 5%–35% dry solids. For algal feedstocks, this could mean that some water needs to be removed, whereas for woody biomass, this means adding water to create a slurry (IRENA, 2016). HTL of woody biomass would require pretreatment, such as size reduction and alkaline treatment—which is a means of using acids to remove lignin without degrading the other carbohydrates—in order to obtain a pumpable and stable slurry (Kim, Lee, & Kim, 2016).

Chemistry of the conversion

During HTL, the biomass is subjected to a temperature in the range of 250°C–375°C and a pressure between 5 and 28 megapascals, with water acting both as a solvent and reaction medium (Tian, Li, Liu, Zhang, & Lu, 2014). At this temperature and pressure, the water remains in a liquid state. As reported by Biller and Ross (2016), three main steps occur:

1. Hydrolysis of macromolecules into smaller fragments;
2. Conversion into smaller compounds by dehydration and decarboxylation;
3. Rearrangement into larger, hydrophobic macromolecules via condensation, cyclization, and polymerization (i.e., producing bio-crude).

HTL does not require a catalyst, especially if the feedstock is high in nitrogen, but adding a catalyst could theoretically improve the process's

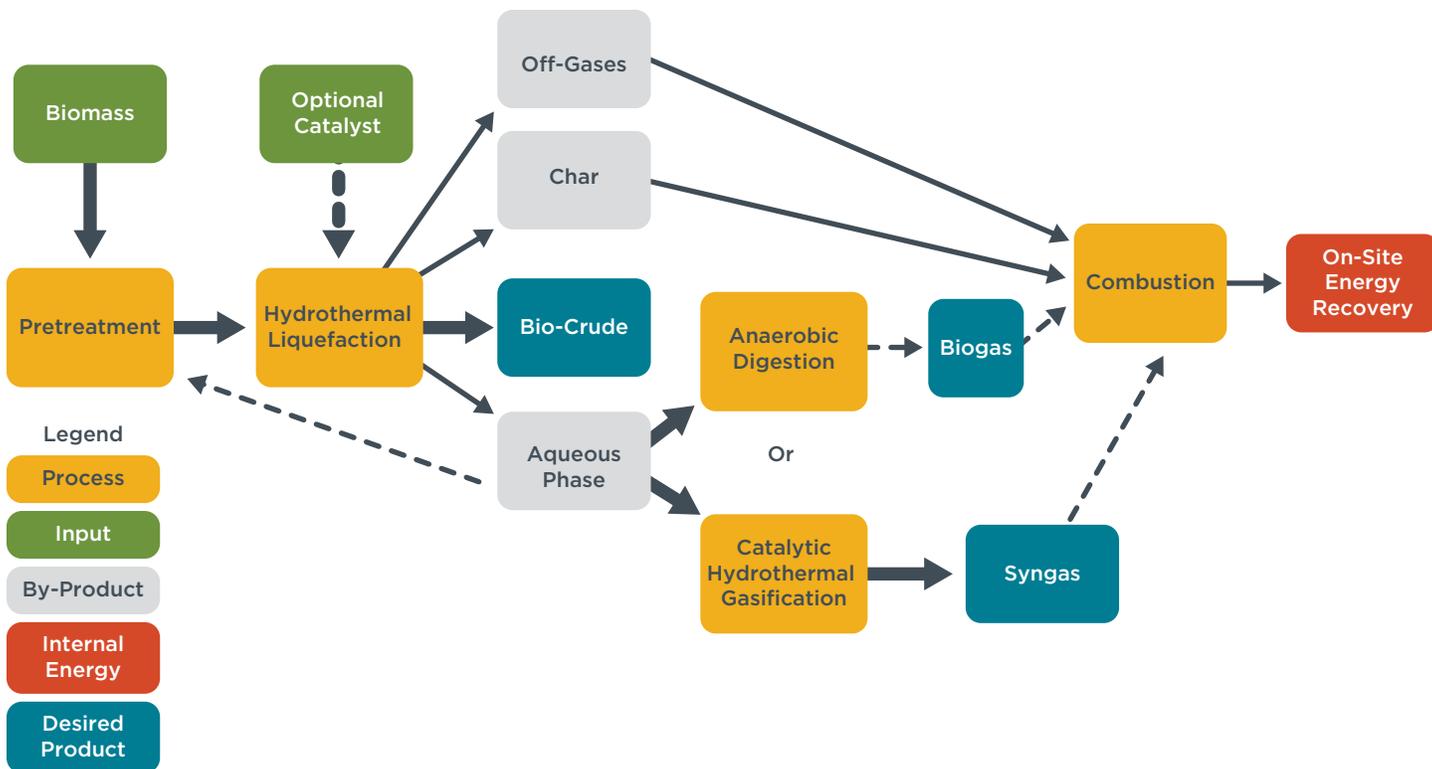


Figure 7: Simplified overview of hydrothermal liquefaction.

efficiency and suppress the formation of some undesirable products (IRENA, 2016). In particular, alkali catalysts have been beneficial for improving yield and bio-crude quality from lignocellulosic feedstocks.

Reactor system

Currently, research has focused on batch reactors, but continuous reactor systems have higher throughput and lower residence times than batch operation, increasing total reactor output and reducing energy requirements. An important consideration for commercial HTL producers will be how to balance operating at lower residence times while still achieving the desired chemical energy recovery (Biller & Ross, 2016).

Final product and upgrading

The bio-crude from HTL contains organic compounds with a variety of

molecular weights, influenced largely by feedstock composition and operating conditions. Before it can be used as a transport fuel, it requires deoxygenation and denitrogenation (Tian et al., 2014). This can be achieved through hydrotreating, which is addressed in the Hydroprocessing section. Hydrotreating is also necessary for the bio-oil resulting from pyrolysis, but pyrolysis bio-oil and HTL bio-crude are two very different products. Bio-crude from HTL contains less water and oxygen, making it more viscous but less dense (Biller & Ross, 2016). Bio-crude could also be used as a feedstock for co-refining in an existing fossil refinery to produce energy and chemicals (Tian et al., 2014). Further research and development would be needed for using continuous upgrading facilities (Biller & Ross, 2016).

COMMERCIAL POTENTIAL

While it has some potential advantages relative to other conversion pathways, HTL is not a mature technology; there are no commercial-scale projects currently in operation. Techno-economic analyses have found that feedstock price and product yield are two important factors for the minimum fuel selling price (Biller & Ross, 2016).

Research suggests that biowaste, lignocellulosic wood, and MSW all can be converted to bio-crude oil using the HTL process. HTL could be a particularly attractive technology to convert algae to bio-crude, given the ability of the process to handle feedstocks with very high water content, such as algal streams. Further, HTL produces higher yields of fuel given the same amount of feedstock, compared to other technologies that process only the lipid fraction of algal biomass to produce biofuels, such as hydroprocessing and

transesterification. However, because the upstream barriers for microalgae mass cultivation remain steep, at the moment hydrothermal processing of other feedstocks, particularly biowaste, is more promising (Biller & Ross, 2016).

HTL has several unique advantages. Using pressurized, non-vapor water as a reaction medium enhances mass transfer, and because the water is not converted to steam, this greatly reduces the latent loss of energy, thus increasing the energy efficiency of the reaction. Further, it is possible that by manipulating operating conditions, the process could self-regulate product separation, whereas in other conversion processes additional rectification or extraction is usually necessary (Tian et al., 2014). Another major advantage for HTL is its potential flexibility, as the process can use feedstocks with qualities that can be difficult for other technologies to handle, such as moisture content, heterogeneity, and ash content (Biller & Ross, 2016).

There are several demonstration-scale HTL projects around the world. In Denmark, a small pilot project can process 20 liters per hour with SCF's catalytic liquefaction technology. In 2011, Licella, in partnership with Virgin Australia and Air New Zealand, established a demonstration plant producing jet fuels using a catalytic hydrothermal reactor processing wood and other biomass (Tian et al., 2014). Additionally, Sapphire Energy Inc., based in the United States, and Muradel Pty Ltd., based in Australia, are two companies working on HTL from microalgae. Muradel began operating a \$10.7 million, 30,000 liter-per-year plant to demonstrate its technology converting algae to crude oil at an industrial scale in 2014 (ETIP Bioenergy, n.d.-b).

Biller and Ross (2016) suggest that continuous reactors, particularly

plug-flow reactors, are the most promising type for HTL at the commercial scale. The authors report that since 2010, there have been five continuous reactors reported in the literature, ranging in maximum potential capacity from 13 liters per day at a pilot project at Aarhus University up to 700 liters per day, with 10% by weight slurry, at the University of Sydney. Other institutions, such as the Pacific Northwest National Laboratory (PNNL) and the University of Illinois, are evaluating the suitability of a variety of other feedstocks, including algae, manure, and lignocellulosic biomass at the research scale.

OBSTACLES TO COMMERCIALIZATION

IRENA (2016) highlights several difficulties facing HTL: (a) expensive alloy materials are necessary for the process equipment necessary to avoid corrosion; (b) high pressures can damage system components; and (c) moving and stirring large volume of biomass slurry may create technical problems. There may be potential for improvements through better catalyst performance.

HTL consumes high volumes of water; while generally this is not a problem on the input end, it produces similar volumes of wastewater, which often contain a large amount of organic matter, leading to high wastewater treatment or processing costs (IRENA, 2016). Some researchers have proposed a system where an algal biorefinery reuses and recycles nutrients, wastewater and chemicals; i.e., the HTL wastewater is cleaned and reused in algae cultivation (IRENA, 2016). However, some of the wastewater contains oxidative and toxic compounds that inhibit algae regrowth and thus cannot be recycled (Tian et al., 2014). Although research is ongoing to assess the potential for HTL

wastewater for anaerobic digestion or catalytic hydrothermal gasification, an optimal solution has not yet been identified (IRENA, 2016).

Hydroprocessing

Feedstocks utilized and chemistry of the conversion

Hydroprocessing is an overarching term for a refining process with several separate chemical processes—hydrotreating, hydroisomerization, and hydrocracking—that can be used to prepare biofuels for use as “drop-in” fuels, with characteristics similar to their fossil fuel counterparts. Although hydroprocessing as a means of treating crude oil is an established technology within the conventional refining industry, its use for treatment of biofuels is a relatively recent development. This process can be applied to fast pyrolysis bio-oil, hydrothermal liquefaction bio-crude, and heavier hydrocarbons from Fischer-Tropsch synthesis, all of which are addressed in previous sections, as well as to raw vegetable or waste oils and fats.

Hydrotreatment removes atoms other than carbon and hydrogen (e.g., oxygen, nitrogen) and saturates double bonds by reacting fuel streams with hydrogen in the presence of a catalyst. The hydrogen combines with these heteroatoms and they are removed as volatile hydrogenated compounds. These non-hydrocarbons (e.g., water and off-gases) are then separated from the upgraded hydrocarbon oil. The light gases go to the hydrogen plant as feed, and the oil is fed into a fractionator column to obtain gasoline and diesel (Thilakarathne, 2016).

Hydrocracking is used to break down low-value heavy oil fractions, which is to say those with longer carbon chains, into higher value products with shorter carbon chains, such as gasoline, by

applying hydrogen to the crude fuel mix at high temperatures and pressures in the presence of a catalyst. For example, waxes from Fischer-Tropsch synthesis can be hydrocracked into lighter hydrocarbon fractions, such as gasoline and diesel, to increase the final yield of valuable products.

Waste oils, vegetable oils, and fats, such as tallow, can be converted into drop-in diesel or jet fuel substitutes using a combination of both hydroprocessing technologies. These finished fuels are typically referred to as renewable diesel, hydrogenation derived renewable diesel (HDRD), or hydrotreated vegetable oil (HVO). A similar middle distillate, hydroprocessed esters and fatty acids (HEFA) fuel, can be produced for use in aviation. The resulting hydrocarbons can be further hydrocracked into shorter chains depending on the desired outputs for the process.

COMMERCIAL POTENTIAL

Hydroprocessing-derived renewable diesel from fats and oils already is considered a mature pathway that is produced at a commercial scale, showing that there is potential for hydroprocessed fuels from other feedstocks to reach this level of commercial maturity. Because of the potential for integrating hydroprocessing with conventional petroleum refining, co-refining is considered to be a promising route for advanced fuels production.

At least 10 plants worldwide produce renewable diesel using hydroprocessing, which together produced around 4.5 billion liters in 2014 (IEA Bioenergy, 2018). HEFA fuel for aviation already has been ASTM-certified as a drop-in alternative jet fuel and is being produced at commercial scales (Kharina & Pavlenko, 2017). High-freeze point HEFA, or HEFA+, is another hydroprocessing-derived

alternative jet fuel that is also nearing ASTM certification at a lower blend rate than standard HEFA, but may be cheaper to produce than conventional HEFA (Pavlenko & Kharina, 2018).

Neste, which is headquartered in Espoo, Finland, is the largest renewable diesel producer in the world. It also was the first company to successfully develop a commercial-scale HVO production process, using its NEXBTL technology. In total, Neste facilities have about 2.6 million tonnes capacity, costing roughly \$1.7 billion in total investment (Lindfors, n.d.). Neste operates two plants in Finland processing 200,000 tonnes per year that each cost around \$115 million to construct. In Singapore and Rotterdam, Neste operates facilities that cost around \$630 million and \$770 million, respectively, to construct, which both process 1.1 million tonnes per year (Neste, personal communication, June 15, 2018).

In Italy, Eni SpA was the first company in the world to transform an existing oil refining plant into a biorefinery, which it says required a capital expenditure of \$123 million, compared to \$638 million for a greenfield project (Mawhood, Gazis, de Jong, & Hoefnagels, 2016). It uses Ecofining technology.

Diamond Green Diesel, in Norco, LA, operates the largest commercial advanced biofuel facility in the United States. For that facility, Honeywell UOP and Eni SpA have developed the hydroprocessing method called Ecofining that converts nonedible natural oils and animal fats to drop-in diesel (Lane, 2014a). In 2017, Diamond Green Diesel reported it would be expanding from 10,000 barrels per day (bpd) to 18,000 bpd, producing 1 billion liters per year. In 2017, this project was slated for completion in 2018 (Lane, 2017b).

AltAir uses Honeywell UOP's technology to produce HEFA fuel as part

of its product slate, making it the world's first HVO facility to regularly produce renewable jet fuel at scale. United Airlines agreed to purchase up to 5 million liters of alternative jet fuel a year for three years, starting in 2016 (Kharina & Pavlenko, 2017). To minimize capital costs, AltAir repurposed a former asphalt plant. The retrofitting process cost several hundred million dollars, some of which was paid for by government grants.

OBSTACLES TO COMMERCIALIZATION

For HVO and HEFA specifically, because the production methods are already commercialized, there are no major technology barriers to expanding hydroprocessing capacity. Relative to production capacity, the capital costs for hydroprocessing facilities are substantially lower than for other advanced fuel conversion pathways and there is much greater certainty on product yields ((S&T)² Consultants, Inc., 2018)

Techno-economic assessment estimates that feedstock costs are the single biggest contributor to the prices of HEFA fuels from waste oils (Seber et al., 2014). Thus, it is unlikely that production costs can decline much further (Pearlson, Wollersheim, & Hileman, 2013). Although vegetable oils are an expensive feedstock, waste oil and fat prices are not much lower (U.S. Department of Agriculture Economic Research Service, n.d.). However, Neste has indicated that future research and development efforts will target expanding the feedstock base for its process in order to both expand production and bring down feedstock prices. It is important that these feedstocks include low-carbon, sustainable feedstocks such as agricultural residues, municipal or industrial waste streams, lignocellulosic energy crops, and forestry residues. Additionally, if

the conversion pathways that require hydroprocessing to create drop-in fuels reach commercialization, e.g., Fischer-Tropsch and fast pyrolysis, the need for hydroprocessing finishing facilities also will increase.

Power-to-X

OVERVIEW OF CONVERSION PROCESS

Power-to-X (PtX), which includes power-to-liquids (PtL) and power-to-gas (PtG), is a set of processes that convert electrical energy to liquid or gaseous fuels using either CO₂ or CO as a feedstock. To achieve climate benefits through PtX, the electricity for the process must come from low-carbon, renewable sources such as solar or wind power, and use carbon captured from either industrial flue gases or stack emissions or directly from the atmosphere. The PtX process, rather than one discrete technology, uses a series of separate processes to

combine the energy from renewable electricity with captured carbon to create synthetic fuels.

CHEMISTRY OF THE CONVERSION

Figure 8 shows the primary steps in the PtX process: electrolysis and combining the hydrogen with carbon, through either methanol synthesis, methanation, or reverse water-gas shift. PtX requires external heat and energy, but this figure shows only where there is potential for recycling or exporting energy.

Electrolysis splits water into its elemental components, hydrogen gas and oxygen gas. There are several electrolyzing technologies currently in various states of development or deployment, including alkaline electrolysis, proton exchange membrane (PEM) electrolysis, and solid-oxide electrolyzer cells (SOECs), also known as steam and co-electrolysis. All three technologies allow for the oxygen and hydrogen to

be recovered at very high purity levels. SOECs operate at higher temperatures than the other technologies, 600°C–800°C, and the waste heat can be used for steam generation and reducing total electricity consumption relative to other options (Schmidt, Weindorf, Roth, Batteiger, & Riegel, 2016). Only SOECs produce enough heat to make steam, which can be used as an energy source for electrolysis (see Figure 8).

After electrolysis, the hydrogen must be combined with carbon in order to create a hydrocarbon fuel, such as methane, or a liquid fuel, such as drop-in diesel or gasoline, methanol, or dimethyl ether (DME) (Schmidt et al., 2016). Typically, the carbon in a PtX process comes from carbon dioxide collected from the atmosphere or from a point source. In some cases, the process may also use carbon monoxide captured from steel mills or other industrial processes.

There are two main chemical technologies for CO₂ capture: (a) CO₂ is absorbed

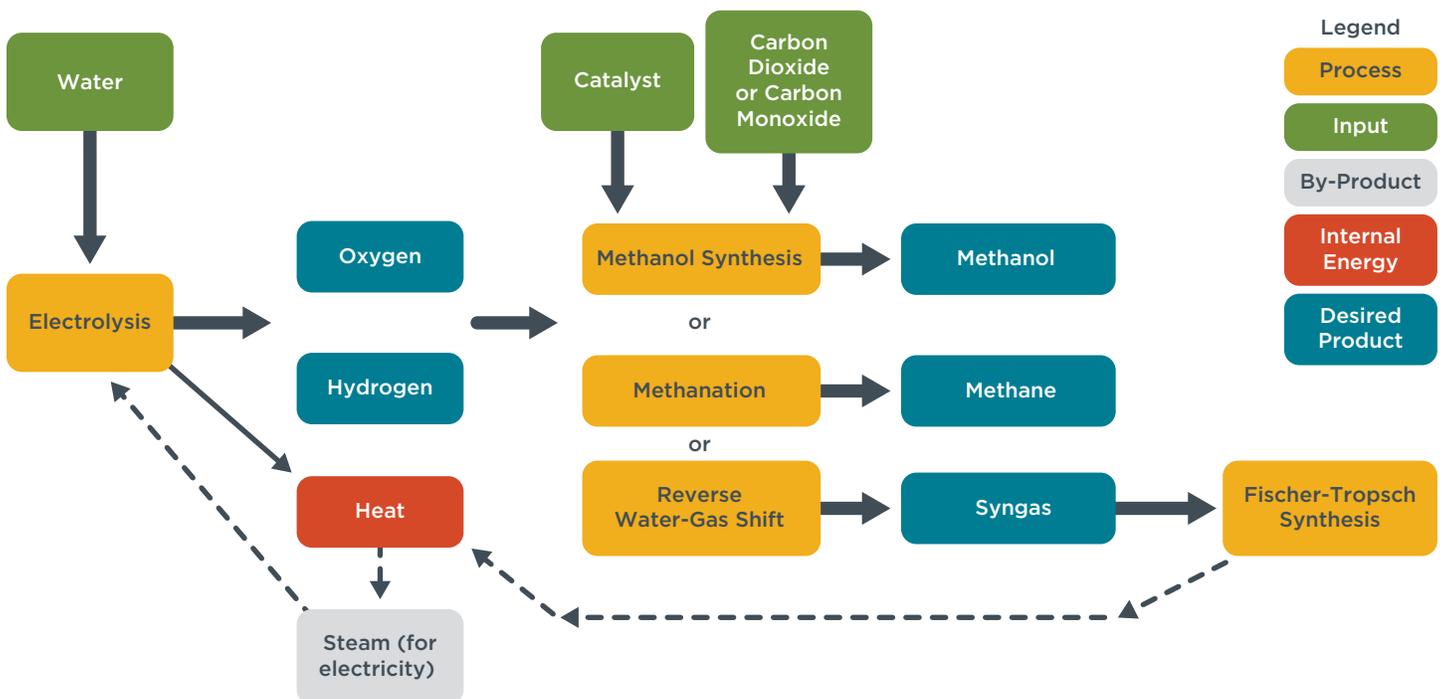


Figure 8: Simplified overview of PtX. Primary steps are highlighted with bold arrows.

onto amines, then recovered by heating the saturated amines, which can then be used again; or (b) calcium hydroxide solution binds CO_2 , forming calcium carbonate (CaCO_3), which is then heated to high temperatures to release the CO_2 , and the residual calcium oxide is returned to the capture solution. Both systems can be used with either point sources of CO_2 , such as industrial flue gases (carbon capture) or with CO_2 recovered from the atmosphere (direct air capture), but the technological readiness of carbon capture at a concentrated source is higher than direct air capture technology (Schmidt et al., 2016). The main differences between carbon capture at a point source and direct air capture are the gas temperatures and the concentration of CO_2 . In particular, flue gases are hotter than air and have a higher concentration of CO_2 than the atmosphere (Jones, 2012). These differences necessitate different operational implementations, but the underlying chemistry is similar.

Once the CO_2 has been collected, the specific chemical process it undergoes with the hydrogen depends on the type of fuel desired. For example, hydrogen could be reacted with carbon dioxide to produce methane or methanol. Methanol can be used in low blends with gasoline (Malins, 2017). As described in Schmidt et al. (2016), there are several processes by which to further convert methanol to drop-in transport fuels: DME synthesis, olefin synthesis, oligomerization, and hydrotreating.

Alternatively, the mixture of CO_2 and hydrogen could be converted into a mix of CO, water, and hydrogen through a reverse water-gas shift reaction. The resulting syngas can then be used as an input for Fischer-Tropsch synthesis and converted to liquid hydrocarbons, a process addressed in an earlier section.

COMMERCIAL POTENTIAL

All of the stages of the power-to-liquid process have been demonstrated, although no existing facilities produce drop-in transportation fuels via this technology (Malins, 2017). These technologies are only now being assembled together into a single process to produce fuels (Schmidt et al., 2016).

Alkaline electrolysis is the most developed and commercially ready step in PtX technology. It has been used in industry for many years and provides a very high degree of hydrogen purity; however, it requires high maintenance. PEM is more reliable and more flexible but also more expensive, and it still requires further development. SOEC has lower electricity needs to produce hydrogen (Badwal, Giddey, & Munnings, 2013). This technology promises the highest electrolysis efficiency and low capital costs, but it still is in the proof-of-concept phase of development (Grond & Holstein, 2014).

Carbon Recycling International has been operating the George Olah Renewable Methanol plant in Iceland since 2012. It is a power-to-liquid process that uses power and CO_2 from a geothermal plant. It appears to be commercially operational, producing 4,000 tonnes of methanol a year, with plans for expansion (Gale, 2016; Extance, 2016).

There are several PtL demonstration plants around the world. Sunfire has a demonstration-scale facility in Dresden, Germany, using SOEC technology and producing synthetic crude oil (Beckman, 2014). Recently the company announced achieving 1,500 continuous hours on-stream, producing 3 tonnes of electrofuels (Sunfire, 2017). The facility is part of a project funded by Germany's Ministry for Economic Affairs and Energy. Sunfire also is in a partnership with Nordic Blue Crude, which is planning a facility in Herøya, Norway (Nordic Blue Crude, n.d.).

In addition, Inerate's Soletair operates a pilot-sized unit, using direct air capture, at Lappeenranta University of Technology in Finland ("Finnish demo plant," 2017). In October 2016, Carbon Engineering and Greystone announced that they were developing a demonstration plant in British Columbia, which will use CO_2 from direct air capture to produce liquid transportation fuels. It is still in its early stages, and project funding comes from the British Columbia Innovative Clean Energy Fund. Carbon Engineering already has a 1 tonne- CO_2 per day air capture pilot plant (Greystone, n.d.).

OBSTACLES TO COMMERCIALIZATION

High production cost is a major barrier to commercialization of PtX (Searle & Christensen, 2018). The primary cost driver for PtX production is the cost of renewable electricity production. The German Umweltbundesamt (Federal Environment Agency) wrote that PtG and PtL plants are not currently economically viable in Germany because of the lack of investment, high operating costs, transformation losses, and framework conditions (e.g., taxes and charges) (Purr, et al., 2016).

Conclusions

The commercial statuses and obstacles facing the conversion technology pathways and upgrading processes reviewed in this paper are summarized in Table 1. Advanced alternative fuels pathways are at varying stages of development, with some having been demonstrated only at the pilot project scale and others having reached commercial maturity. Finishing processes such as hydroprocessing and FT synthesis are already largely commercialized.

For each pathway assessed here, a number of obstacles to commercialization have been identified. The largest

barriers may be political and economic, but there are several technological barriers as well. A critical barrier is the issue of scaling: Across pathways, the literature suggests that reactors for larger-scale facilities may need to adopt different designs than what has been done already at a demonstration scale. Another common obstacle is related to the supply of raw materials, which may be dispersed, leading to high transportation costs, or highly heterogeneous, potentially requiring complex and expensive collection. Finally, pretreatment is a significant cost in advanced alternative fuels production. Although many waste and lignocellulosic feedstocks are cheap to acquire, preparing them for conversion can

be a capital-intensive, expensive, and complex process, making the overall conversion process more difficult.

Several of these obstacles could be overcome in the near future through the deployment of systems that allow for material and energy recovery or otherwise take advantage of economies of scale. For example, the chemical catalysts common in many processes can be expensive to purchase and maintain, but this barrier can be overcome through the use of robust catalysts with longer lifetimes and reactor designs that facilitate more efficient catalyst recovery. Recycling energy and other inputs, as well as co-processing of bio-oil and bio-crude along with conventional petroleum, could also reduce costs, as long

as these can be executed efficiently. For example, some FT facilities use tail gas recycling, and process water can also be recycled during hydrothermal liquefaction. An example of co-processing would be co-refining the bio-oil from fast pyrolysis along with conventional oil in fluid catalytic cracking units. For the production of cellulosic ethanol, some bolt-on facilities are located next to conventional corn ethanol facilities, converting the waste that is left over from the conventional facility. By overcoming these obstacles during the next decade, advanced alternative fuels producers will demonstrate that promising results at demonstration-scale projects are scalable with the right financial and political incentives in place.

Table 1: Summary of the current status and obstacles facing the conversion technology pathways and upgrading processes addressed in this paper

Technology	Status in 2019 for producing advanced fuels	Obstacles to commercialization		
		Pretreatment	Conversion	Upgrading
Cellulosic ethanol	Early commercial	Recalcitrance of lignin and hemicellulose	High-solids loading; cost of enzymes and other chemicals; C5 sugar content	
Gasification	Early commercial, but demonstration for transport fuels production	Grinding, milling, and drying the feedstock	Tar production	Syngas cleaning
Gas fermentation	Demonstration		Maintaining activity rate of microorganisms is energy intensive; bacterial activity is inhibited by by-products; bacterial contamination	
Fischer-Tropsch	Commercial, but demonstration for low-carbon fuels production		Optimization of gasification technology for use with FT; low catalyst selectivity	
Fast pyrolysis	Early commercial for on-site combustion, but demonstration for transport fuels production	Grinding, milling, and drying the feedstock	Heating the feedstock to an appropriate temperature is expensive	High water and oxygen content; bio-oil is corrosive
Hydrothermal liquefaction	Demonstration		Expensive alloy materials are necessary to prevent corrosion of system components; high pressure can damage system components; moving and stirring large volume of biomass slurry may create technical problems and creates high volumes of wastewater	
Hydroprocessing	Commercial (using fats and oils)			
Power-to-X	Demonstration		High electricity input costs in many regions	

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