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Review of Biomass Resources and Conversion Technologies for Alternative Jet Fuel Production in Hawai'i and Tropical Regions

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Ⓢ *Supporting Information*

ABSTRACT: There is increasing interest in developing biobased alternative jet fuels to meet rising aviation demand and address environmental concerns. Uncertainty of oil prices, issues of energy security, and rising greenhouse gas concentrations have spurred the development and acceptance of alternative, economically viable, environmentally sustainable production pathways. The objectives of this study were to review alternative jet fuel feedstock candidates and relevant conversion data to provide a baseline of information to be accessed and built upon in developing production scenarios in Hawai'i and other tropical regions bounded by the Tropic of Cancer in the northern hemisphere and the Tropic of Capricorn in the southern hemisphere. Seventeen plants that produce oil, fiber, and sugar feedstocks were identified, and information on cultural practices, yield ranges, invasiveness, and mechanization status was assembled. Available data on pretreatment requirements and conversion processes for the 17 feedstocks, including mass and energy balances, product and byproduct yield and quality, and scale requirements/unit sizes, were reviewed. This effort seeks to inform the development and design of alternative jet fuel production along regional supply chains in Hawai'i and other locations in the tropics.

1. INTRODUCTION

There is increasing interest in developing alternative jet-fuels (AJF) to reduce the amount of fossil fuels required to meet the increasing demand for liquid fuels (38% AJF by 2025[1]), while reducing environmental pollution, addressing climate change concerns, and security of supply issues.[2−5] AJF produced from biorenewable resources can significantly lower greenhouse gas (GHG) emissions and reduce the carbon footprint of the industry when compared to petroleum derived jet-fuel.[5−7] Further, biofuels have the potential to offer other environmental benefits including improvements in soil quality, water quality, sustainability, and biodiversity.[8] Biofuel production and use can also contribute to improving the security of supply and benefits to the local economy.

Approximately 22 billion gallons of jet fuels, classified as kerosene-type and naptha-type fuels, are produced annually in the United States[9] and about 80 billion gallons per year worldwide.[2] Conventional petroleum derived jet fuel has a boiling point range of 150−290 °C and is composed of a blend of hydrocarbons, typically C8 to C16 linear, branched, and cyclic alkanes and up to ∼30% aromatics, and it is a middle distillate between gasoline and diesel. Aviation kerosene fuel is defined in the American standard test method (ASTM D1655). There are a number of different types of jet fuel such as "fuel oil no. 5" (CAS70892-11-4), kerosene (jet fuel A1, CAS 8008-20-6), and hydro desulfurized kerosene (CAS 64742-81-0).

The airline industry and the Federal Aviation Administration (FAA) have been investigating a transition to alternative fuels produced from a wide range of abundant biomass resources in an effort to reduce dependence on fossil fuels, to improve fuel security,[1] and mitigate environmental impacts.[10,11] According to the United Nations Framework Convention on Climate Change, the airline sector is currently responsible for 3% of total global GHG emissions. Although it is a small fraction, the emissions from the airline industry have been growing rapidly and are expected to reach 5% of global GHG emissions by 2050.[5,12] Sustainable biofuels have the potential to significantly reduce life-cycle GHG emissions in the aviation sector.

Today there are five technologies approved by ASTM (ASTM D7566) to produce AJFs:[13] (1) Hydroprocessed Ester and Fatty Acids Synthetic Paraffinic Kerosene (HEFA-SPK),[14−17] (2, 3) Fischer−Tropsch synthetic paraffinic kerosene (FT-SPK) and FT synthetic kerosene with aromatics (FT-SKA),[16,18−20] (4) Direct Sugars to Hydrocarbons (DSHC), also known as synthesized iso-parafins (SIP),[21] and (5) Alcohol to Jet (ATJ).[22] Other pathways that are under various stages of the ASTM evaluation process are (5) Hydrotreated Depolymerized Cellulosic Jet (HDCJ|UOP, Kior),[23−25] (6) Synthetic Kerosene and Synthetic Aromatic Kerosene (SK&SAK|Virent), and (8) Catalytic Hydro-Thermolysis (CH|ARA[26]). Figure 1 provides an overview of the different schemes and technologies that can be used for the production of alternative jet fuels.

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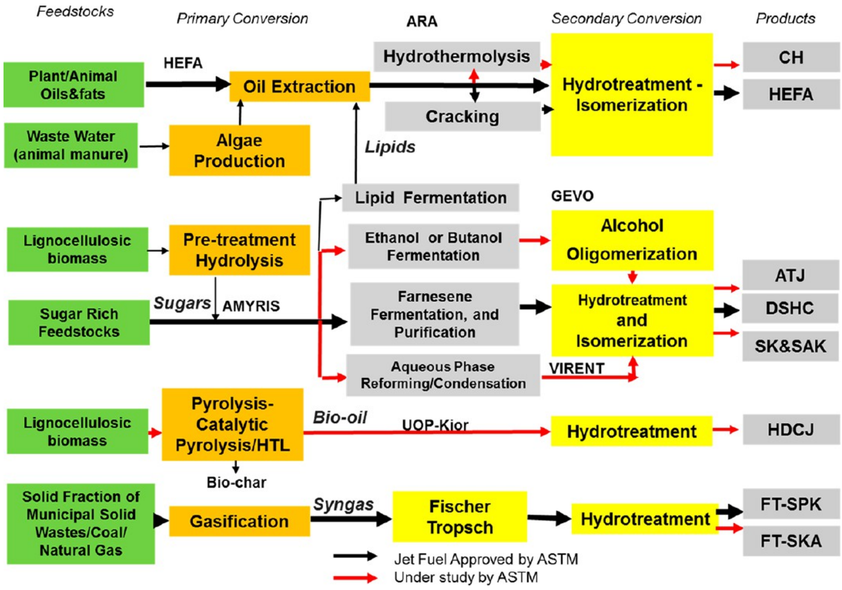


Figure 1. Pathway for the production of alternative jet fuel.

Because there are many potential feedstocks, this review will focus on the those relevant for Hawai'i and tropical regions. The objectives of this review were to (1) evaluate the potential of candidate feedstock crops for AJF production, (2) provide baseline information relevant to developing alternative jet fuel production scenarios for regional supply chains in Hawai'i and tropical regions, (3) investigate some key implications (feedstock ecology and requirements and sustainability issues) related to the use of these alternative biofuels, and (4) review information on the conversion of the identified feedstock into AJF, summarizing technological aspects, feedstock properties, conversion yields, coproducts, and cost estimates where possible.

The first and foremost task was to identify a list of potential AJF candidate crops. Six species (listed below) were identified in a recent "crop assessment" report[27] as having potential for use as energy crops out of a total of 26 types that were investigated: (1) Sugarcane (*Saccharum officinarum* L.), as currently grown on Maui; (2) type I energycane (*Saccharum spontaneum*); (3) type II energycane, a high yielding variety adapted to central Maui; (4) Banagrass (*Pennisetum purpureum x Pennisetum glaucum*); (5) Leucaena (*Leucaena leucocephala*); (6) Eucalyptus (*Eucalyptus*, various species)

An additional eight crops are also included due to their potential as feedstocks for advanced biofuel production. Table 1 lists the 17 crops (species) assessed in this review. The list contains feedstocks that can be grown across various geographic regions in Hawai'i and other tropical locations. The tropics are bounded by the Tropic of Cancer in the northern hemisphere and the Tropic of Capricorn in the southern hemisphere. Both lie ~23.5° of latitude away from the equator and are defined by the northern and southern most point where the sun is directly overhead on the June and December solstices, respectively.

2. AJF CROP CANDIDATES

The following sections describe 17 plants considered as feedstock for AJF production.

2.1. Oil Plants. The following sections describe four plants that produce oils (jatropha, kamani, pongamia, croton) and could be used for AJF production. A summary of the key information regarding growing conditions and oil yields for the four oil crops is provided in section 2.3.

Table 1. Identification List (Common and Scientific Names and Family) of Feedstock Candidate Resources for AJF

no.	crop common name	scientific name	family	feedstock type
1	Banagrass	*Pennisetum purpureum* Schumach	Poaceae	fiber
2	Energycane	(*Saccharum officinarum* X *S. robustum)*	Poaceae	fiber
	Eucalyptus			
3	Bluegum Eucalyptus	*Eucalyptus globulus* Labill	Myrtaceae	fiber
4	Rainbow Eucalyptus	*Eucalyptus deglupta* Blume	Myrtaceae	fiber
5	Robusta Eucalyptus	*Eucalyptus robusta* Sm.	Myrtaceae	fiber
6	Rose gum Eucalyptus	*Eucalyptus grandis* W. Hill ex Maiden	Myrtaceae	fiber
7	Saligna Eucalyptus	*Eucalyptus saligna* Sm.	Myrtaceae	fiber
8	Gliricidia	*Gliricidia sepium* (Jacq.) Kunth ex Walp.	Fabaceae	fiber
9	Leucaena hybrid	*Leucaena*-KX$_4$	Fabacaea	fiber
10	Rice (husks and straw)	*Oryza sativa* L.	Poaceae	fiber
11	Sorghum	*Sorghum bicolor* L.	Poaceae	fiber
12	Sesbania (Ohai)	*Sesbania grandiflora* (L.) Poir	Fabaceae	fiber
13	Sugarcane	*Saccharum officinarum* L.	Poaceae	sugar and fiber
14	Jatropha	*Jatropha curcas* L.	Euphorbiaceae	oil
15	Kamani	*Calophyllum inophyllum* L.	Clusiaceae	oil
16	Pongamia	*Pongamia pinnata* (L.) Pierre	Fabaceae	oil
17	Croton (Musine)	*Croton megalocarpus* Hutch.	Euphorbiaceae	oil

2.1.1. Jatropha.

Jatropha curcas L. is a nonedible, multipurpose plant (Figure 2) that is considered to be one of the more promising crops for biodiesel production because it does not compete directly with food production, has the potential to grow on degraded soil, and is resistant to drought and pests.[28−30] As of 2010, Brazil has over 40 000 ha of jatropha cultivation with significant crop development undertaken by the federal agricultural research organization (EMBRAPA).[31] The authors point out however that although jatropha is typically considered to thrive in poor quality land and require few inputs (irrigation, fertilizer), this is rarely the case in practice.

Figure 2. *Jatropha curcas* L. at Poamoho Research Station, Waialua, Hawai'i (left) and jatropha seeds (right).

Jatropha is native to Central America and Mexico but now thrives in most tropical and subtropical regions of the world,[32,33] with cultivation limits at 30° N and 35° S. It also grows in lower altitudes of 0−500 m above sea level. It is not sensitive to day length (flowering is independent of latitude) and may flower at any time of the year.[34] The optimum rainfall for seed production is 1000−1500 mm and optimum temperatures are 20−28°C.[35] The best soils are aerated sands and loams of at least 45 cm depth.[36] Jatropha has ability to grow in alkaline soils (soil pH 6.0−8.5).[37] Plant densities range from 1100 to 2500 plants ha^{-1}.[38] There are 3 seeds per fruit and it takes 3−4 months after flowering to mature.[39]

Seed yields vary based on genetic provenance (varieties), age, propagation method, pruning, rainfall, tree spacing, and soil type or soil fertility. Jatropha has a pattern of high oil production[40] and can continue yielding for 40 years.[41] With good sites (fertile soil and average annual rainfall 900−1200 mm) and optimal management practices, yields of 5.0 Mg dry seed ha^{-1} $year^{-1}$,[42−44] and 6.0−7.0 Mg ha^{-1} $year^{-1}$[135] have been reported. The seed oil content can range from 18.4 to 42.3%,[34] typically 30−35%. The oil has been identified as a suitable feedstock for biodiesel production.[45,46] Jatropha plantations are managed through weeding, pruning, and thinning to reach a final density of 400−500 trees ha^{-1} when the trees are mature.[37,38]

The seed oil can be used as a feedstock for biodiesel, soap fabrication, glue or dye industry, pesticides, paints, lubricating oils, and for medical applications.[47] Extracting oil from dry seeds may be accomplished by mechanical (engine-driven press can be used to extract about 70−80% of oil) and chemical methods (using a solvent such as *n*-hexane can extract 95−99% of the oil).[38] There are three important byproducts from jatropha biodiesel production: seed husk, seed cake, and glycerol. The seed husks (removed before oil extraction) can be used for direct combustion and as feedstock for gasification.[48] The residue seed cake that remains after oil extraction from seeds and kernels contains high-quality proteins (unsuitable as a fodder), is rich in nitrogen and phosphorus, and can be used as manure (fertilizer) to enhance soil organic carbon.[49,50] The glycerol (byproduct from the transesterification of oil into biodiesel) can be used to produce heat by combustion, and in the cosmetic industry, soaps and other products.[38] The analysis of the air-dried seed shows the following composition: moisture 6.2%, protein 18%, fat 38%, carbohydrates 17%, fiber 15.5%, and ash 5.3%. The oil contains 21% saturated fatty acids and 79% unsaturated fatty acids.[51]

Manual harvesting of jatropha and tools to improve labor productivity have been assessed.[52] On a common basis, productivity estimates spanned an order of magnitude, ranging from to 16 to 140 kg seed day^{-1} based on an 8 h work day. Everson et al.[53] suggested that manual harvesting in South Africa would not be cost-effective and that mechanized harvesting would be required. Manual harvesting also has issues due to toxicity/irritation. Jatropha's asynchronous flowering and the resulting presence of fruit on the tree in all states of maturity at any given time adds challenges to mechanical harvesting. Mechanical harvesters such as the Korvan 9240 have been tested.[52]

It was found that, the renewable energy in the form of biodiesel produced from jatropha can emit 80% less CO_2 and 100% less SO_2 than fossil diesel.[44] Bailis and Baka[31] reported a life cycle analysis (LCA) and GHG emission study for jatropha hydrotreated renewable jet fuel (HRJ) fuel produced in Brazil, including the effect of land use changes. The data for jatropha was based on surveys of Brazilian farmers and processors. The mass balance for HRJ for jatropha reported that 177 kg of dry fruit (seeds and husks) produced 46.7 kg of semirefined oil that yielded 22.6 kg of HRJ equal to 1 GJ of energy. Based on a dry fruit yield of 4 tons per hectare per year, the use of drip irrigation and an assumed 20 year plantation lifetime with no direct land use changes, the GHG emission were ~55% lower than for conventional jet fuel.[31] However, the GHG emission varies significantly depending on land use changes; in the best case, an 85% reduction could be achieved, but in the worst case, a 60% increase resulted.[31]

2.1.2. Kamani.

Calophyllum inophyllum L. Kamani (Figure 3) grows in warm climates along coastal areas and low land forests, although it occasionally occurs inland at higher elevations. It is a native of eastern Africa, southern coastal India, Southeast Asia, Australia, and the south Pacific.

Figure 3. Kamani trees (left) and kamani fruit (right) from University of Hawai'i, Manoa campus.

The tree grows in tropical areas including the Hawaiian and Pacific Islands and subtropical climates close to sea level with a mean annual rainfall of 1000−5000 mm.[54] The trees are sensitive to frost and fire. Wind and salt tolerance makes it suitable for sand dune stabilization.[55] Kamani tolerates a wide range of soils. It grows well in drained, light to medium soils (sands, sandy loams, loams, and sandy clay loams), and acid to neutral soil with pH of 4.0−7.4.[54,56] Kamani is a well-known ornamental plant species with medicinal properties. Leaves, bark, flowers, fruits, and seeds are used in traditional practices and for the treatment of skin diseases, wounds, ulcers, etc.[57,58]

It is a moderately fast growing tree that can attain a height of 1 m tall within a year, can be grown in mixed cultures, and does not require weeding. Kamani is easy to propagate by seed. Fruits are usually borne twice a year, and it produces up to 100 kg of fruits tree^{-1} year^{-1} and about 18 kg of oil.[59] Ripe fruit are most easily collected from the ground under the tree, and a healthy tree produces annually around 8000 fruits which contain a kernel within a hard husk (Figure 4). The kernels extracted from the fruit have a dry weight of about 5 g, which translates to ~40 kg of kernels tree^{-1} year^{-1}. With 400 trees per hectare (5 m × 5 m spacing),[60] a total of 16 Mg of kernels per hectare can be produced annually. These kernels contain about 25−60% useful oil on a unit dry mass basis with an average of ~30%; therefore, each tree can yield approximately 18.4 kg of oil, resulting in about 4.8 to 7.2 Mg ha^{-1} year^{-1} of oil.[54]

Figure 4. Ripe kamani fruit with cracked shell showing the seed kernel inside.

To extract the kernels, the nuts need to be cracked (Figure 4). Seed processing, drying, and oil extraction methods have a significant impact on oil yields. The seeds need to be dried in order to allow the oil to form and condense.[61] Kernels will turn from creamy white to brown during this process. The oil can be extracted by cold-pressing and filtration; and it was found that seed preparation had a significant impact on oil yields. Kernels dried to 15% moisture content provided the highest oil yields.[61] The cultivation of kamani oil can be considered a potential renewable energy source, and the oil could be transesterified. Limited information is available about production of biodiesel from kamani oil, and no information was found on AJF production.

2.1.3. Croton (Musine).

Croton megalocarpus Hutch (Figure 5) is an indigenous tree in East and South Africa which has recently attracted interest as a biofuel source because of its high oil yield.[62] It is widespread in Tanzania, Kenya, and Uganda between the altitudes of 1300 and 2200 m with an annual rainfall between 800 and 1600 mm and average annual temperatures between 11 and 26 °C. It requires a light, deep, well-drained soil.[62]

Figure 5. Croton tree at Ho'omaluhia botanical garden, Honolulu, Hawai'i (left) and croton fruits (right).

As a fast growing tree, croton has a wide range of uses such as fuelwood and charcoal, fence posts and poles (because of its termite resistance), shade, wind protection, and soil conservation.[63] Other parts of the tree such as bark, seeds, roots, and leaves are used as medicine (to treat stomach ailments, malaria, wounds (clotting), and pneumonia),[64] bee forage, mulch, or green manure.[65,66] The species propagates well through seedlings, and under favorable climatic conditions may sometimes become invasive.[66]

C. megalocarpus produces 5−10 Mg seeds ha^{-1} year^{-1}.[67] The seeds from East Africa have a composition of 30−32% oil and 18−50% protein.[67,68] Croton has been identified as a potential large scale resource for biodiesel production that will not compete with food crops.[62,69]

2.1.4. Pongamia.

Pongamia or *Milletia pinnata* (L.) Pierre (Figure 6) is a nitrogen-fixing tree, native in tropical and temperate Asia including India, China, Japan, Myanmar, Malaysia, Nepal, and Thailand, where it has a long history of uses in traditional medicine, as an oil source, as animal fodder, and other purposes.[70] It is native in northern Australia and has been recently established in other parts of Australia and other humid tropical lowlands including the USA.[66] It has been characterized as invasive[71] or moderately invasive and not an immediate problem[72,73] depending on the classification system used.

Figure 6. Pongamia tree at University of Hawai'i-Manoa campus, Honolulu, Hawai'i (left), flowers (middle), and seedpod (right).

Pongamia can grow from sea level to altitudes of approximately 1200 m with optimal annual rainfall from 500 to 2500 mm, maximum temperature of 38 °C, and minimum temperature of 16 °C. Pongamia grows well on most soil types ranging from stony to sandy to clay, although it does not do well in dry sands. It is tolerant to salinity and drought.[66] It can be propagated either by seeds or by root suckers.[74] Trees often reach adult height in 4 or 5 years, bearing fruit at the age of 4−7 years when grown from seed. Seed yield potential ranges from 900 to 9000 kg ha^{-1} (assuming 100 trees ha^{-1}), and oil averages 25% of seed content.[75,76] Pongamia has three coproducts: (1) seed oil that is suitable for conversion to liquid fuels such as biodiesel; (2) high-protein seed cake make it suitable as organic fertilizer, while its use as animal feed remains under investigation;[70,77] and (3) pods suitable for combustion. Ortiz-Martinez et al.[78] reported the major fatty acid composition of pongamia crude oil as palmitic acid 11.79%, stearic acid 6.53%, linoleic acid 19.35%, oleic acid

52.57%, linolenic acid 3.88%, arachidic acid 1.35%, gadoleic acid 1.12%, and behenic acid 3.23%. The oil-rich seeds, the oil characteristics (fatty acid composition), and the seed's inedibility make pongamia a potentially attractive energy crop.[29,70,75,78,79]

2.2. Fiber Feedstock. Lignocelluosic biomass, a renewable and widely distributed resource, is increasingly used for the production of biofuels.[7] Various tree and grass species that grow in Hawai'i and other tropical regions have been assessed for their potential as AJF resources. The fuel properties for all the fiber crops covered in this review are provided in the Supporting Information Section S1. A summary of the fiber yields for all the candidate crops is displayed in section 2.3.

2.2.1. Gliricidia. *Gliricidia sepium* (Jacq.) Kunth ex Walp (Figure 7) is a widely cultivated multipurpose N-fixing tree, native to tropical dry forest in Mexico and Central America.[80] It is cultivated as forage in many tropical and subtropical regions including the Caribbean, northern parts of South America, central Africa, parts of India, southeast Asia, the Pacific Islands, and in southern Florida.[81−83]

Figure 7. *Gliricidia sepium* tree (left) at University of Hawai'i-Manoa campus, Honolulu.

Gliricidia (Figure 7) can tolerate a wide variety of soils including volcanic, sandy, clay, and limestone soils. It also grows well in acidic soils with a pH of 4.5−6.2.[82,84] Gliricidia grows best in warm, seasonally dry climates with annual rainfall of 900−1500 mm and elevation up to 1200 m.[82] It does not tolerate cooler temperatures and high elevation.[85] It can be easily propagated by cuttings and seeds[86] and has been used for fuel,[82] shade, green manure, living fences, construction poles, fodder, bee forage, biofuel, and other purposes.[83,87]

Short-rotation coppicing is the normal and preferred system for maximizing biomass production of gliricidia. Coppicing can be carried out at fixed intervals, usually of 1−3 years, and both unpruned and periodically pruned trees can fix atmospheric N_2. Pruning intensity affects nodulation,[88] and it was found that 54% of total N was fixed from the atmosphere by gliricidia during the 6 months of regrowth following pruning.[89] Application of gliricidia mulch and manure can improve soil fertility and moisture availability because the leaves decompose rapidly releasing N and K.[86,90] As a green manure, it has been estimated that 15 Mg ha^{-1} $year^{-1}$ of leaf biomass can provide the equivalent of 40 kg ha^{-1} $year^{-1}$ of nitrogen. Gliricidia has been reported to have high nutritional value as a protein supplement for animals such as cattle, sheep, and goats.[91] Furthermore, gliricidia has been used for medicinal purposes including treatment of bruises, burns, colds, coughs, fever, ulcers, antibacterial activity, and other medical issues.[66,87] Gliricidia's leaf extract can be a potential natural larvicide against mosquitoes and can be an alternative to commercial mosquito pesticide.[92]

Gliricidia planted as fuelwood/fodder resources can provide 15−30 Mg ha^{-1} $year^{-1}$ fresh total biomass when densely planted, intensively harvested in a continuously cropping cycle. Stewart et al.[93] reported 5−6 Mg ha^{-1} $year^{-1}$ dry biomass planted at 2 m × 2 m (2500 trees ha^{-1}) spacing in Central America with stems around 15 cm in diameter. However, in Tanzania, the average mean annual wood increment of gliricidia in a 5-year-old rotation was 5.83 Mg ha $year^{-1}$.[94]

2.2.2. Sesbania or Ohai'ula'ula. *Sesbania grandiflora* L. Poir is a pan-tropical, fast-growing tree (Figure 8), native to tropical Asia including India, Sri Lanka, Indonesia, Malaysia, Myanmar, Philippines, and Northern Australia, and is now widespread in most humid tropical regions of the world.[91,95,96]

Figure 8. *Sesbania grandiflora* tree.

It has been traditionally used in medicine as antidiabetes, antioxidant, antipyretic, and expectorant and in the management of various ailments.[96] Sesbania has been adapted to the lowland tropics, up to 1000 m above sea level with a mean annual temperature range of 22−30 °C.[91] Although it can adapt to high annual rainfall conditions of 2000−4000 mm and tolerate flooding over short periods, the optimum growth is in the semiarid areas with ~800 mm annual rainfall and up to 9 months dry season.[97] Sesbania can grow in a wide range of soils including heavy clay, alkaline, poorly drained, saline, or low fertility and has some tolerance to acid-soils down to pH 4.5.[98] The tree establishes rapidly from seed or by vegetative propagation from stem and branch cuttings, can attain a height of 5−6 m in 9 months in fertile sites, and has a potential lifespan of 20 years.

Sesbania can be planted at high densities (up to 3000 stems ha^{-1}) to produce pole timber or to produce dry-season forage and fuelwood. This species cannot survive frequent cutting management systems (pollarding), so careful cutting is essential for sustainable production.[99] An annual yield of 27 kg of green leaf tree^{-1} can be achieved by harvesting side branches every 3−4 months, and a green manure yield of 55 Mg ha^{-1} green material in 6.5 months was reported for Java, Indonesia.[66,91] However, if the trees are cut back to a suitable height, a large supply of fresh fodder can be obtained for most of the dry season.[100] In terms of forage quality, ref 101 reported that *S. grandiflora* contained more crude protein but less fiber than *Gliricidia sepium* and *Leucaena leucocephala*; associated dry matter digestibilities were 73.3, 65.2 and 62.2%, respectively.

The calorific value of *S. grandiflora* wood is 17.91 MJ kg^{-1}, with an ash content of 6%.[66] At a very short rotation of 3−4 years, the tree can produce much higher fiber raw material per unit area than most other pulp woods (on a 3-year rotation, about 41 Mg ha^{-1} year^{-1} of pulp can be harvested, basis not reported). Sesbania trees planted at 90 cm intervals, at a density of 12 000 plants ha^{-1} can yield 50−100 Mg of leaf material ha^{-1} year^{-1}, about 75% of which is water, suggesting dry matter (DM) yields of 12−25 Mg ha^{-1} year^{-1}. However, the yields have typically ranged from 4 to 12 Mg of DM ha^{-1} year^{-1}, depending upon location.[66] The clear gum from the bark is used in foods and adhesives as a substitute for arabic gum, and the bark yields tannins as well.[66]

2.2.3. Giant Hybrid Leucaena. *Leucaena*-KX4 has been particularly popular because of its N-fixing abilities and multiple uses.[102] It can grow up to 20 m in height. The multipurpose species is used to produce livestock fodder, fuelwood, timber, mulch, and human food in agroforestry systems throughout the tropics.[103−106] The kernel of seeds contain more than 20% oil (basis not reported), and it can be used as a feedstock for biofuel production or can be directly blended with the fossil fuel at the maximum of 20%.[105] The seed oil can also be converted into biodiesel by transesterification.[105,107] The seeds may also be used as feed concentrates for dairy animals, as manure,[108] and as a protein source.[109] New hybrids of leucaena such as "KX2 and KX4-Hawai'i" (Figure 9) have been bred to be largely self-sterile.[105] Self-seediness is associated with invasiveness and can reduce wood and fodder yields.

Hawaiian giant types "KX4-Hawaii" is a tropical, seedless leucaena developed at the College of Tropical Agriculture and Human Resources of the University of Hawai'i. It is a sterile triploid hybrid between *Leucaena leucocephala* X *L. esculenta* and can grow rapidly to 15 m in 5 years.[110] It has proved to produce high biomass yields in short rotations and has potential also for use as a coppiceable, high-value hardwood grown on 8 to 12-year rotations.[110]

In their native range, leucaena spp. grows on shallow limestone soils, coastal sands, and seasonally dry, self-mulching vertisol soils of pH 7.0−8.5. In exotic locations, they require well-drained soils with pH above 5.0 where aluminum saturation is very low. In general, the hybrids are intolerant of soils with low pH, low P, low Ca, high aluminum saturation and are sensitive to high salinity and waterlogging.[105,110] Optimum growth will be achieved in subhumid and humid climates with annual rainfall of 1000−2500 mm and up to 3500 mm in environments with no distinct dry season. However, reasonable growth will be achieved in drier environments (above 600 mm year^{-1}). For optimum growth, a temperature of 25−30 °C is required and growth ceases below 14−15 °C. Very high forage yields have been recorded for leucaena especially the hybrid (i.e., KX2-hybrids) in southeast Asia, Australia, and Hawai'i, producing 15 Mg of DM ha^{-1} year $^{-1}$.[105,106]

Figure 9. Six month *Luecaena*-KX4 at Hawaiian Commercial & Sugar Co., Maui, Hawai'i.

Hybrid KX4-Hawai'i is psyllid-resistant, can grow to a mature height of 15 m in 6−8 years, and is strongly arboreal. Brewbaker[110] reported that 10-year-old trees grown at normal 2.5 m × 3 m spacing appear to be economically harvestable as hardwood with greater than 25 cm diameter and 0.6 specific gravity. The fast growing KX4-Hawai'i hybrid can produce 15−20 Mg of DM ha^{-1} year^{-1} in Hawai'i (unpublished data), and strong stem regrowth potential after coppicing can make this sterile hybrid a good candidate for biofuel production.

2.2.4. Eucalyptus (Gum Tree). There are more than 700 species of eucalyptus. Most are native to Australia, and a very small number are found native in adjacent areas of New Guinea and Indonesia. Eucalyptus is one of the most widely grown hardwoods in the world. Species of eucalyptus are cultivated in the tropical and temperate world.[111] Eucalyptus species have the potential to provide sustainable and low cost woody feedstock because of their rapid growth and adaptability to a wide range of climates.[112,113] Commercial plantations of eucalyptus are found from Hawai'i to South Africa. The average productivity of South Africa eucalyptus (mainly *Eucalyptus grandis*) is 21 m^3 ha^{-1} year^{-1} (the density is not reported; therefore, it is not possible to estimate the mass yield), hence there is great interest in eucalyptus as an energy feedstock globally.[114,115] Eucalyptus plantations are generally planned to operate on short rotations (5−10 years).

Five eucalyptus species, *E. deglupta*, *E. globulus*, *E. grandis*, *E. robusta*, and *E. saligna*, were selected as candidates for fiber production because of their high biomass production over a range of environments found in Hawai'i and the tropics.

2.2.4.1. Bluegum Eucalyptus. *Eucalyptus globulus* Labill is native to Tasmania and southeastern Australia. The native latitudinal range is 38° 26′ S to 43° 30′ S.[116] It is the most extensively planted eucalyptus species in the world[117] because of its rapid growth and adaptability to a range of conditions.[118] Blue gum eucalyptus grows well in cool high elevations of the tropics.[119,120] In the United States, it is present in Hawai'i and California where it has naturalized.[121,122] In its native zone, the maximum temperature is 20−23 °C with minimum temperature of 0−8 °C and a mean annual rainfall of 600−1400 mm.[123] It grows well on a wide range of soils and requires good drainage, low salinity, and soil depth of 60 cm or more.[120,124] In Hawai'i, the tree grows very well on Typic and Hydric Dystrandepts and soils of the latosolic brown forest great soil group. These soils are generally 0.9 m (3 ft) deep, acid in reaction, and formed on volcanic ash.[125]

Blue gum is an attractive choice for dimensional lumber, furniture, fuel wood, bioenergy, medicinal uses, cleaning products, and for reforestation and afforestation efforts.[126] Its high growth rate, short rotation length (10 years), and favorable pulpwood properties make it the world's most important commercial source of paper and fiber[127] and is a major source of fuelwood in many countries because of its ability to coppice. The wood burns freely, leaves little ash, and produces good charcoal.[120] A wide range of growth and yield figures are reported in the literature. For instance, in Australia-Tasmania, the volumetric yield at 17 years was 35 m^3 ha^{-1} $year^{-1}$ with tree height of 30 m.[121] In Victoria, Australia, blue gum in a closely spaced, fertilized plantation yielded a mean annual increment (MAI) of 9−14 Mg ha^{-1} dry weight of stem wood at 4 years.[128] Sochacki et al.[113] reported average biomass yields of 16 Mg ha^{-1} from 4000 trees ha^{-1} in a 3 year rotation (5.3 Mg ha^{-1} $year^{-1}$). Average stem wood dry weights were 5 to 7 Mg ha^{-1} $year^{-1}$ in 3−6 year old coppiced stands in Hawai'i. An average annual yield of 10−15 m^3 ha^{-1} $year^{-1}$ is considered as an achievable yield for this species over large areas.[116,129] Blue gum eucalyptus plantations are usually coppiced two or three times on 8−12 year rotations.[127]

2.2.4.2. Rainbow Eucalyptus. Eucalyptus deglupta Blume is one of the few eucalyptus species not occurring in Australia and has a natural distribution from Indonesia, Philippines (Mindanao), and Papua New Guinea.[127] It is widely planted throughout the humid tropics, where it is one of the most important eucalyptus, thriving in tropical settings that receive plentiful rain.[66] In the U.S., rainbow eucalyptus grows in the frost-free climates like Hawai'i and the southern portions of California, Texas, and Florida. It can grow through elevations from 0 to 1800 m above sea level, with a mean annual temperature between 23 and 31 °C and mean annual rainfall of 2500−5000 mm. It can grow successfully on coarse-textured sands and loamy soils, volcanic ash, and limestone-derived soils (pH 6−7.5). Best growth occurs on deep, moderately fertile, well-drained, sandy alluvial loams with adequate soil moisture.[66] Growth rates are excellent on suitable sites (25−40 m^3 ha^{-1} $year^{-1}$ over 15 years in Papua New Guinea), and the wood and bark are good sources of pulp fiber.[116] Yields of 20−40 m^3 ha^{-1} $year^{-1}$ are common in several countries.[130] The Philippines and Indonesia, followed by Brazil, have the most extensive plantations.[116]

E. deglupta is extremely frost-sensitive, is very susceptible to fire, does no coppice readily, and is susceptible to a variety of pests and diseases.[116] Stands 2−4 years of age in Costa Rica produce MAIs ranging between 2 and 39 m^3 ha^{-1} $year^{-1}$, and the maximum MAI recorded was 89 m^3 ha^{-1} $year^{-1}$ over a 4.5 year period.[131] In pulpwood plantations yields of 200−300 m^3 ha^{-1} at 10−12 years of age are commonly achieved. Palma and Carandang[132] have estimated 24.4 Mg of DM ha^{-1} $year^{-1}$ as the annual yield from rainbow eucalyptus.

2.2.4.3. Robusta Eucalyptus. Eucalyptus robusta Sm. is native along the Australian coast of New South Wales and southeast Queensland. The species has been introduced into many tropical, subtropical, and warm-temperate climates including Puerto Rico, southern Florida, coastal California, and Hawai'i,[133,134] has established successfully over a remarkable range of environments from equatorial regions to an approximate latitude 23° N and 35° S, and is naturalized in southern Florida and Hawai'i.[135] It is highly tolerant to seasonal waterlogging and prefers soils with typically heavy clays but also light sandy clays.[123] It grows well on sites in the moist tropics up to an elevation of 1600 m. Preferred conditions include a mean annual temperature of 23 °C and rainfall in excess of 1500 mm distributed fairly uniformly throughout the year.[136] It can withstand average minimum temperatures of 3 °C.[137] This species has a wide ranging physiological adaptability and may establish successfully on sites of much lower rainfall, a minimum of 700 mm. Mature trees are remarkably tolerant of frost.[138] In Hawai'i, robusta eucalyptus grows well from near sea level to 1100 m where annual rainfall ranges from 1000 mm to 6350 mm and temperatures rarely if ever reach freezing. Although robusta eucalyptus can recover from occasional severe frost damage, the limiting variable in its distribution seems to be low temperature.

E. robusta provides a moderately durable hardwood with an air-dry density of 805−900 kg m^{-3} for wood from natural stands in Australia and 725−800 kg m^{-3} for plantation timber in Hawai'i.[139] In Argentina, 5-year-old stands measured 9 m tall (1583 trees ha^{-1}) and had a basal area of 10 m^2 and a volume of 89 m^3 for an average of 18 m^3 ha^{-1} $year^{-1}$. Webb et al.[140] reported wood yields of 14−28 m^3 ha^{-1} $year^{-1}$. *Eucalyptus robusta* can yield 13.0 Mg of DM ha^{-1} $year^{-1}$ and can exceed 20.0 Mg of DM ha^{-1} $year^{-1}$.[141]

2.2.4.4. Rose Gum Eucalyptus. Eucalyptus grandis W. Hill ex Maiden is native to the east coast of Australia where the annual rainfall varies from 1100 to 3500 mm.[142] The climate in the Australian native range is humid subtropical with minimum temperatures of 2 to 10 °C and a maximum of 29 °C.[129] It can grow well on moist, well drained, deep, fertile alluvial loamy soils.[142] Rose gum eucalyptus is a fast growing species in short rotations with an average height growth of 4 m $year^{-1}$.[143] In Brazil, the wood yield from *E. grandis* at age 5 years can reach 107 Mg of DM ha^{-1} for rain fed and 141 Mg of DM ha^{-1} for irrigated plantations.[144] The mean annual yield is about 27 m^3 ha^{-1} $year^{-1}$.[129] A hybrid of rose gum eucalyptus was also reported to produce 22−27 Mg of DM ha^{-1} $year^{-1}$ in Brazil.[145] *E. grandis* is considered a good biofuel feedstock due to its short rotation, high biomass production, high wood density, and resistance to pest and disease.[146]

Wood and bark bulk densities are 0.45 and 0.32 g cm^{-3}, respectively. The moisture content of wood and bark are 50 and 72%, respectively.[147]

2.2.4.5. Saligna Eucalyptus. Eucalyptus saligna Sm. is native to the coastline of New South Wales and south coast and central Queensland-Australia. It is a fast growing hardwood reaching 55 m heights in its natural habitat.[148] There are large plantations of this species in many parts of Africa (Angola and South Africa), South America (Brazil), and the Pacific (Hawai'i).[149] It grows well in cooler climates; for example, northern New Zealand[120] and the uplands of Hawai'i.[150] Its natural zone is between latitudes 28° and 35° south, with a mean annual rainfall of 800−1800 mm and a mean annual temperature of 14−23 °C.[66] Saligna eucalyptus usually grows on moderately fertile moist loam, well-drained soils, alluvial sandy loams, and other soils including volcanic loams.[66]

Saligna eucalyptus is an important multipurpose hardwood used for firewood, charcoal, timber, furniture, veneer, bee forage, and flooring.[151] It is considered to be a promising biofuel resource for second-generation processes.[152] The average biomass yield from 10 year rotations of Saligna eucalyptus on the Island of Hawai'i with 2500 tree per hectare was 155 Mg of DM ha^{-1} (15.5 Mg of DM ha^{-1} $year^{-1}$).[153] The average volume increment in stands under 25-year rotations on sustainable sites was between 36 and 53 m^3 ha^{-1} $year^{-1}$. Nicholas and Hall[154] estimated the wood density and yield of oven dry stem wood from *E. saligna* to be 610 kg m^{-3} and 20.6 Mg ha^{-1} $year^{-1}$, respectively.

2.2.5. Banagrass. The hybrid of Pennisetum purpureum Schumach, also known as napier or elephant grass, originated in Africa, is a C_4 perennial grass (C_4 refers to plants that cycle CO_2 into four carbon sugars), and lives in hot moist or arid nonsaline habitats. C_4 plants are more photosynthetically efficient than the C_3 plants[155] and can produce high biomass yields (Figure 10). Banagrass is also known for its high nutrient and water use efficiency.[156,157] It has been introduced to most tropical and subtropical countries in South America, Asia, and Africa where annual moisture ranges from 750 to 2500 mm rainfall.[158] Under favorable soil and climate conditions, banagrass can be ratooned for multiple years with high biomass output.[159] Ratooning (no-till) is a common practice around the world[160] in which the lower part of the plant and living roots are left after harvesting and the subsequent crop regrows from them. The soil is undisturbed and accumulates soil organic carbon improving soil aggregation and fertility and potentially contributes to the sustainability of the entire production system.[157,161] Trials in the Southeast USA have recorded dry mass yields above 25 Mg ha^{-1} $year^{-1}$ for the first two ratoon crops followed by a decline in yields for subsequent seasons.[156]

Figure 10. Six month old banagrass at Waimanalo Research Station, Hawai'i.

This species has been found to out-perform sugarcane and other feedstock species in dry matter biomass production under comparable irrigation and fertilizer regimes.[162] Recent studies have shown that several varieties of napier grass (which includes banagrass) can utilize biological nitrogen fixation, allowing them to maintain high biomass yields without significant fertilizer application by fixing atmospheric N_2 to a useable form of ammonia (NH_3).[162]

Yields of irrigated and unirrigated banagrass on soils suitable for sugar production in Hawai'i were estimated to be 49 and 40 Mg of dry fiber ha^{-1} $year^{-1}$, respectively.[163] Because of its robust growth, it is considered one of the most valuable forages and is grown widely across the wet tropics.[158] It is also considered as a potential bioenergy crop in several countries including Thailand, the Philippines, China, Australia, and the United States. Since its original introduction from Australia to Hawai'I in the mid-1970s, banagrass has been used locally as windbreaks. More recently, studies have been carried out to determine its performance during fast pyrolysis,[164,165] gasification (publication in preparation, Cui and Turn, HNEI), flash carbonization (for metallurgical bio carbon production),[166] and as a bioethanol feedstock.[167,168]

The potential yield of banagrass depends on many factors including environmental conditions such as climate and soil, together with management choices including irrigation and fertilization. Tran et al.[168] reported a yield of 48.19 Mg ha^{-1} $year^{-1}$. The average dry matter (DM) yield in Kenya of most napier varieties is 15−40 Mg ha^{-1} $year^{-1}$. At harvest, banagrass on average contains 20% DM and 8−10% crude protein, 70% NDF (neutral detergent fiber) and 45% ADF (acid detergent fiber).[169] However, banagrass has provided as much as 45 Mg of DM ha^{-1} $year^{-1}$ on irrigated land due to its rapid growth, which allows for multiple harvests each year.[156] One of the most productive C_4 vegetative species ever reported was a banagrass grown in El Salvador, which produced 88 Mg of DM ha^{-1} $year^{-1}$.[157,170]

2.2.6. Sugar. Saccharum officinarum L. (Figure 11) is a widely cultivated tropical perennial C_4 crop that has evolved through selections from the two wild species *S. spontaneum* and *S. robustum*. It is of African origin characterized by very high levels of sugar (>20% sucrose) in its sap and can grow to over 5 m in height.[171−173] Sugar cane is well-known for supporting a drought-resistant, robust root system that can improve soil structure and accumulate carbon on marginal lands.[174,175] Sugar cane produces two useful AJF feedstocks, sugar and fiber.

2.2.6.1. Sugar. Sugarcane has a long history of cultivation in Hawai'I dating back to the 1800s and was grown to produce sugar, molasses, and bagasse as byproducts. Molasses was marketed as cattle feed supplement but can be used as a feedstock for ethanol production. The sugars extracted from sugarcane can be easily fermented to produce ethanol, a first-generation biofuel. Sugar cane was identified as one of the most promising candidate species for biofuel production in Hawai'i and other tropics because of its rapid growth, drought tolerance, and high yields.[176,177]

In Hawai'i, the average dry biomass yield of sugarcane ranges from 40 to 80 Mg ha^{-1} $year^{-1}$ (which consists of about 60% fiber and 40% sugar) and up to 86.2 Mg ha^{-1} $year^{-1}$ in

Figure 11. Two year old sugarcane at Hawaiian Commercial & Sugar Co. Plantation, Kahului, Maui, Hawai'i.

Brazil.[176,178] Sugarcane in Hawai'i has been grown as a biennial crop, reaching maturity after 24 months. Due to the recumbent plant architecture at this age, harvest techniques included open burning of fields to remove dead leaves and tops prior to windrowing and grapple loading cane into trucks for transport to the processing factory. This destructive harvest system was followed by deep tillage and mechanized planting of the subsequent sugarcane crop. Land was not rotated into other crops in the Hawai'i sugarcane production system.

2.2.6.2. Bagasse. Bagasse is the wet fibrous matter that remains after sugarcane stalks are crushed to extract their juice and can be used to produce cellulosic ethanol, a second-generation biofuel.[108] Bagasse is a term applied to the plant fiber and its inherent moisture post sugar extraction. Bagasse is utilized as a biofuel (combustion), in the manufacture of paper pulp,[179] and to produce building materials such as medium density fiberboard.

For each 10 tons of sugarcane crushed, a sugar factory produces nearly 3 tons of wet bagasse at 40−50% moisture content. Since bagasse is a byproduct of the cane sugar industry, the quantity of production in each country is commensurate with the quantity of sugarcane produced. The high moisture content of bagasse, typically 40−50%, requires consideration for it to be effectively utilized as a fuel. In general, bagasse can be stored prior to use or further processing and this is typically done in open or covered piles. A typical chemical analysis of bagasse (from Maui, HI) is cellulose 39.2%, hemicellulose 20.2%, lignin 25.5%, ash 4.2−7.6%, and waxes <1%.[180]

Sugar cane bagasse is a potentially abundant source of energy for large producers of sugarcane, such as Brazil, India, and China.[108] In Brazil, sugarcane has been used for ethanol production for decades and supplies 40−50% of the country's transportation fuel.[157,181] Somerville et al.[157] estimated sugarcane ethanol yields of 6900 L ha^{-1}from sugar, 3000 L ha^{-1}from bagasse, and 9950 L ha^{-1} total, compared with average corn grain ethanol yields of 2900 L ha^{-1}. Furthermore, in Brazil, the sugarcane bagasse is often burned for the generation of electricity.[148]

2.2.7. Energycane. *Saccharum officinarum* X *S. robustum* (Figure 12) is the term used to describe hybrids of *Saccharum sp.* that have been selected for high biomass, high fiber, and low sucrose concentration. Due to high biomass productivity and noninvasiveness, energycane has great potential as feedstock for second generation cellulosic ethanol. Like sugarcane, energycane is a tall (more than 3 m) perennial C$_4$ grass grown in the relatively frost-free areas of the southernmost states (Florida, Louisiana, Texas, and Hawai'i) where there is plentiful rainfall or irrigation. It is planted by stem cuttings (seed cane) and harvested about every 12 months by green cane harvesters.

Figure 12. One year (2nd ratoon) of energycane at Hawaiian Commercial & Sugar Co., Kahului, Maui, Hawai'i.

Average energycane yields (DM) are much higher, but brix (sugar) levels are lower, compared with commercial sugarcane. The fiber content of energycane is approximately double that of sugarcane.

Leal[182] raised concerns about the differences between sugarcane and energycane and their impacts on sugar extraction (water consumption, energy requirements, and extraction efficiency) and steam consumption. Energycane contains ∼54% juice (wet basis). The juice contains approximately 10% of total sugars; the major sugar was sucrose (9.6%).[183] The fiber consists of ∼37.0% cellulose, ∼14.7% hemicellulose, and ∼22.7% lignin.[165]

Dry biomass yields of energycane ranged from 26.9 to 31.4 Mg ha^{-1} year^{-1} in Florida.[108] In Hawai'i, the above-ground and below-ground biomass for the plant crop of energycane harvested after 1 year were 40.78 and 4.63 Mg ha^{-1}, respectively (unpublished data).

2.2.8. Sorghum. *Sorghum bicolor* L. (Figure 13) is cultivated in warmer climates worldwide. Commercial sorghum species are native to tropical and subtropical regions of Africa and Asia. It is thought to have originated in Ethiopia and has spread to other parts of Africa, India, Southeast Asia, Australia,[184] and the United States. Latitudinal limits are 40° N and S. It can be grown at altitudes from sea-level to 1000 m where annual rainfall ranges from 400 to 750 mm.

Sorghum is an important C$_4$ grass and the fifth most produced cereal crop worldwide.[185,186] Sorghum has high

Figure 13. Three month old fiber sorghum (hybrid SS506) at Hawaiian Commercial & Sugar Plantation, Kahului, Maui, Hawai'i.

biomass yield and excellent nitrogen use efficiency.[187−189] After harvesting, most varieties will regrow or ratoon. The ability to form a ratoon enables multiple harvests per season in some climates although the ratoon crop yields typically decrease. It is cultivated for its grain, sugar-rich stem juice, and/or forage biomass depending on the type of sorghum (grain sorghum, sweet sorghum, or forage sorghum) and is gaining increasing research interest as an annual bioenergy crop.[185,190] Forage sorghums are generally categorized as taller sorghums that have lower stalk sugar content than sweet sorghums and are generally harvested as silage.[191] FAO reported the USA was the top producer of grain sorghum in 2009, with a harvest of 9.7 million tons. The next four major producers of sorghum, in decreasing quantities, were India, Nigeria, Sudan, and Ethiopia. The other major sorghum producing regions in the world, by harvested quantities, were Australia, Brazil, China, Burkina Faso, Argentina, Mali, Cameroon, Egypt, Niger, Tanzania, Chad, Uganda, Mozambique, Venezuela, and Ghana.[192]

Sorghum can tolerate a wide range of soil conditions, from heavy clay soils to light sand, with pH ranging from 5.0 to 8.5.[193] It usually grows poorly on sandy soils, except where heavy textured subsoil is present. Sorghum is more tolerant of alkaline salts than other grain crops and can therefore be successfully cultivated on soils with a pH between 5.5 and 8.5. Soils with clay percentage between 10 and 30% are optimal for sorghum production.

Sorghum cannot be planted until soil temperatures have reached 17 °C. The long growing season, usually 90−120 days, causes yields to be severely decreased if plants are not in the ground early enough. Yields have been found to be boosted by 10−15% when optimum use of moisture and sunlight is achieved by planting with a 25 cm row spacing instead of the conventional 1-m row. Temperature (27−30 °C) plays an important role in attaining optimum growth and development after germination. Sorghum is a short-day plant, which means that the plant requires short days (long nights) to trigger the reproductive stage. The optimum photoperiod, to induce flower formation, is between 10 and 11 h. Photoperiods longer than 11−12 h delays flowering. Tropical varieties are usually more photoperiod sensitive than short-season varieties. Sorghum plants are most sensitive to the photoperiod immediately following the juvenile phase.

In recent years, there has been renewed interest in sorghum's use as a potential feedstock for cellulosic ethanol production, mainly due to the ability of some varieties to produce large quantities of biomass with minimal inputs. Generally, the yield and quality characteristics of forage crops are determined by the harvesting stage, genotypes, management practices, and environmental factors.[194] This is because interactions between genotype, stage of maturity at harvest and growth pattern, heavily influence forage yield, and nutritive value.[195] In China, Zhao et al.[196] reported dry biomass yields of 13.2−35.2 Mg ha^{-1} year^{-1} across five sweet sorghum cultivars. Reported yields of rain fed sorghum ranged from 7.6 to 17.5 Mg ha^{-1} year^{-1} and under irrigation ranged from 15.4 to 21.3 Mg ha^{-1} year^{-1}. Dual purpose forage sorghum dry matter yields during the same trial years ranged from 6.4 to 13.7 Mg ha^{-1} year^{-1} for rain fed and 14.3 to 19.5 Mg ha^{-1} year^{-1} under irrigation.[197,198]

2.2.9. Rice.

Oryza sativa L. commonly known as Asian rice, was first cultivated in southeast Asia, India, and China.[199] Current cultivation for *O. sativa* extends from latitude 35° S (New South Wales and Argentina) to 50° N (Northern China), over 110 countries. Rice is primarily grown in tropical and subtropical climates as an annual plant, although in some tropical areas it can survive as a perennial and can produce a ratoon crop for up to 30 years.[200] The rice plant can grow to 1−1.8 m tall, occasionally more depending on the variety and soil fertility. More than one crop of rice can be grown per year in tropical climates and with ample water availability (e.g., Mekong Delta in SE Asia). This also means that straw is generated more than once a year. The main rice producing areas are located in Southern and South-East Asia: China, India, Indonesia, Bangladesh, and Vietnam.[192]

Rice can grow in a wide range of soil types, including saline, alkaline, and acid-sulfur soils, and the soil chemical properties are not as important as the physical ability of the soil to maintain flooded conditions.[201]

Rice requires temperature above 20 °C but not more than 35−40 °C.[202] The traditional method for cultivating rice is flooding the fields while planting the young seedlings or shortly thereafter. Although flooding is not mandatory for the cultivation of rice, all other production methods require higher effort in weed and pest control during growth periods and a different approach for fertilization.

Rice yields are highly variable, depending on variety, soil, and climate conditions. The average rice yields in Australia and the U.S. in 2010 were 10.8 Mg ha^{-1} and 8.3 Mg ha^{-1}, respectively.[192] China's world record for rice yield is 19 Mg ha^{-1}.[203]

The cultivation of rice results in two types of residues, husks and straw, that have been widely used for heat and/or energy production via combustion. Rough rice and paddy are terms used to describe harvested rice that is encased in the husk. Both husk and straw can be used as feedstock for a variety of energy application such as pyrolysis, liquefaction, gasification, and ethanol production, although these applications are still at the research/demonstration phase of development.[180] Finding a viable pathway for the utilization of rice husk and straw will reduce the negative effects of open disposal that is often practiced and provide an additional source of income for farmers.

2.2.9.1. Rice Husk.

The husk is the main byproduct from rice milling, representing about 20−22% (wt) of the harvested rough rice. Roughly 80% (dry weight) of the raw husk is made of organic components, the remainder is ash (mostly silica compounds).[204,205]

During rice refining processes, the husks are removed from rice grains. It is not useful to feed either human or cattle

Table 2. Agro-Climatic Resources Information for All Candidate Crops Reviewed from the Literature and Global Agro-Ecological Zones (GAEZ Site)[a]

candidate crop	yield	location	latitude	longitude	rainfall (mm)	temp (°C)	growing period (days)	ref
Croton	10	Kagera, Tanzania	−5.51	32.71	705	23	180−209	67
Jatropha	5	Managua, Nicaragua	11.83	−85.75	1400	26.6	220−239	42
Kamani	4.8	Java, Indonesia	−7.14	108.69	2311	24	300−329	209
Pongamia	4.9	Baramati Maharata, India	18.65	−73.5	2656	24.2	150−179	75
Banagrass	40	Waimanalo, Hawai’i	21.39	−157.78	1298	24.1	282	163
Bluegum Eucalyptus	35[b]	Tasmania, Australia	−41.09	145.32	1415	11.6	264	119
	13−44[b]	Santiago, Chile	−32.31	−71.53	372	15.1	187	210
Energycane	26.9−31.3	Florida, USA	25.82	80.49	1258	24.1	282	108
Gliricidia	5.3	Morogoro, Tanzania	−8.94	36.82	1598	25.1	210−239	94
Leucaena hybrid	15	Waimanalo, Hawai’i	21.39	−157.78	1298	24.1	282	105
Rainbow Eucalyptus	24.4	Misamis, Philippines	7.69	124.78	2003	24.2	365	132
	39[b]	Huetarnorte, Costa Rica	10.85	−48.65	1700	26.5	240−269	211
Rice	22.4	Lalanda, Bihar, India	26.34	85.62	1149	24.9	180−209	212
Robusta Eucalyptus	10−35[b]	Madagascar	−15.78	48.27	2057	23.7	300−329	120
Rose gum Eucalyptus	22[b]	Dehra Dun, India	31.83	75.72	1425	22.6	210−239	213
Saligna Eucalyptus	20.6	Hilo, Big Island, Hawai’i	19.54	−154.98	3040	22.5		214
Sorgham	20	Northern Territory, Australia	−15.6	132.99	741	26.6	120−149	215
Sesbania	20−25[b]	Java, Indonesia	−7.01	108.96	2401	25.48	300−329	130
Sugar cane	40−80	Maui, Hawai’i	20.57	−156.69	1305	22.1		176

[a] The yield and location columns are from the references shown in the last column, while latitude, longitude, rainfall, temperature, and growing period (days) were created from the GAEZ site. [b] Yield estimated as m^3 ha^{-1} $year^{-1}$(mass yield data not available), and the others are estimated as Mg ha^{-1} $year^{-1}$.

because of its high silica content. Incorporation of rice husk into the soil mixture was found to have a positive effect for many crops as an organic amendment (such as cowpea).[62,206] Rice husks could become a valuable source or amorphous silicon due to their high ash content (up to ∼20 wt % of the dry husk) which is typically composed of ∼90% silicon dioxide.[180] Rice husk is a processing residue that may be utilized as fuel if quantities are sufficient. In total, 5 Mg of rice paddy are required to produce 1 Mg of rice husk, and it takes approximately 100 000 Mg of rice husk per year to fuel a 10 MW power plant. The world potential production of bioethanol from rice husks is estimated to be 20.9 to 24.3 billion L $year^{-1}$.[207] Rice husk is a significant resource produced in abundance in the countries of Southeast Asia. Fritsche et al.[192] argued that using rice husks as bioenergy or biofuel feedstock had low or near zero land use change risks.

2.2.9.2. Rice Straw. The rice straw to paddy ratio ranges from 1.0 to 4.3.[205] Although the technology for rice husk utilization is well-established worldwide, rice straw is sparingly used as a source of renewable energy. The energy content of rice straw is around 14 MJ per kg at 10% moisture content. The reasons for the limited use of rice straw in energy applications include difficulties and costs involved in collection and transport. Its seasonal production also results in peak periods of availability and requires storage if a year round stable supply is to be provided for an energy conversion facility.

The global production of rice straw amounts to 600−900 million Mg $year^{-1}$.[208] Relative to other agricultural byproducts, it contains a high amount of inorganic components and ash (typically 15−20 wt % dry basis) that reduces its quality as a biofuel feedstock. For large-scale off-field utilization, straw is baled by self-propelled baling machines. At a smaller scale, straw may be manually collected and removed from the field. If straw is not collected but left in the field, it is often open field burned to suppress rice diseases and for rapid disposal. The latter is often necessary to prepare for the subsequent crop when multiple crops per year are possible or because harvest is followed by a rainy season that will render the straw unmanageable if it remains in the field. Due to the large volume of straw, tillage to incorporate the straw can be difficult. Alternatives to open field burning are of continued interest primarily to ameliorate its environmental impacts.

Rice straw typically contains 37.5−47.4% cellulose, 24.3−29.7% hemicellulose, 13.5−16.5% lignin, as well as a number of minor organic and inorganic components.[180] There are two particular challenges when it comes to utilizing rice straw in energy applications. The high carbon-to-nitrogen content (due to low amounts of nitrogen) leads to a very low biodegradability in comparison to other agricultural residues. This is of particular interest when straw is used for anaerobic digestion to produce biogas. It means that in many cases, straw needs to be blended with other agricultural residues, in order to speed up the degradation of organic constituents contained in straw. Another challenge, in particular for thermal processes such as combustion and gasification, is the high ash content, in particular, high amounts of chlorine, sulfur, and potassium.[180] For rice straw, ash concentrations of 18−20% (on dry matter basis) are common. Strengths and weaknesses for rice straw use as a feedstock are summarized below:

Strengths: (1) Rice straw is available in many countries around the world and is one of the most abundant agricultural residues in the world (next to corn and sugarcane residues). (2) Straw as a crop residue is generally not in competition with other uses and has low to negative economic value. Straw is a “nonfood” feedstock that does not play a large role in current food or animal feed markets. (3) Straw exhibits high cellulose content. (4) Positive environmental impact of using straw.

Weaknesses: (1) There are high costs associated with collection, handling, and transport of straw. (2) Straw has a

Table 3. Yield, Invasiveness Status, and Mechanization Categories of AJF Candidates

candidate resources	feedstock type	yield Mg ha^{-1} year^{-1}	AJF yield L ha^{-1}	oil content %	invasive status	mechanization	refs
Croton (Musine)	oil	10	2400	30−32	yes[a]	no	67
Jatropha	oil	5	2000	30−35	yes[c]	yes	35,46
Kamani	oil	4.8	1440	30	no[b]	no	209
Pongamia	oil	4.9	1238	25	yes[c] and no[d]	no	75
Banagrass	fiber	40−49			yes[c]	yes	163
Blue gum eucalyptus	fiber	5−7			yes[c]	yes	129,210
Energycane	fiber	26.9−31.3			no	yes	108
Gliricidia	fiber	5−6			no[c]	no	93
Leucaena hybrid	fiber	15			no[e]	yes	105,110
Rainbow eucalyptus	fiber	24.4			no[c]	yes	132
Rice (Husks)	fiber	2.4−4.2			no	yes	192,205
Rice (Straw)	fiber	2.7−4.8			no	yes	192,205
Robusta eucalyptus	fiber	13			no[c]	yes	141
Rose gum eucalyptus	fiber	22			yes[c]	yes	213
Saligna eucalyptus	fiber	20.6			yes[c]	yes	154
Sorghum	fiber	20			no[c]	yes	215
Sesbania (Ohai)	fiber	4−12			no[c]	no	66
Sugar cane (bagasse)	fiber	10			no[c]	yes	157
Sugar cane	sugar	40−80			no[c]	yes	176

[a] Croton is invasive according to Maroyi.[221] [b] Kamani is not invasive according to Friday and Okano.[54] [c] The Hawai'i-Pacific Weed Risk Assessment List.[71] [d] Pongamia is not considered an immediate problem.[72] [e] Hybrid Leucaena-KX4 is low risk invasiveness according to Brewbaker.[110]

high carbon to nitrogen ratio and low biodegradability (a high carbon to nitrogen ratio is only problematic for biological conversion, not for thermochemical processing). (3) The ash composition of straw could require pretreatment, making it a less favorable feedstock compared to wood or biomass grasses as fuel (in particular for thermal conversion). (4) Nutrients are extracted from the field when straw is collected on an annual basis.

2.3. Summary of Candidate Crops.

The sustainability of future alternative jet fuel production may require the diversification of biomass feedstock resources. In particular, there is a need to optimize utilization of agricultural residues and identify new plant production systems for dedicated feedstock supply. The latter case is more relevant to Hawai'i, which has excellent environmental conditions for producing various bioenergy crops and a substantial amount of fallow land previously used for agriculture. A year-round growing season and strong solar insolation generate high yields from a variety of trees, crops, and grasses.

Important limitations of biobased production systems are the seasonality of biomass production and water availability. Plant growth can be seriously reduced under water-limiting conditions, and the energetic and environmental benefits of bioenergy crops can be affected. In this regard, the humid tropics have favorable temperature and rainfall conditions for plant growth throughout the year, making this region potentially important for bioenergy crop production. However, with the exception of sugarcane, there is limited information about dedicated bioenergy feedstocks that are adapted to conditions in the humid tropics.

The Global Agro-Ecological Zones (GAEZ) Website was used along with maps related to agro-climatic resources to coordinate the geographic location for specific yield data of each candidate included in this report. This information was used to determine the latitude, longitude, rainfall, temperature, and growing period (days) at each location which is summarized in Table 2. This provides high-level yield and climate condition pairings relating productive capacity in the tropics to climate zone.

Nonedible oil candidates (croton, jatropha, kamani, and pongamia) may have more potential as sustainable feedstocks for AJF production compared to edible oils (such as palm and soy).[216,217] Current research is taking place on second generation biofuels which are targeted at addressing the "Food versus Fuel" debate.[216]

Oil production potential was reviewed for four candidates (croton, jatropha, kamani, and pongamia) using three criteria: seed yield (Mg ha^{-1} year^{-1}), AJF yield (L ha^{-1}), and oil content (%) (Table 3). Oil content and seed yield are important criteria in determining the potential for oil production. A good oil-bearing plant must have a high acreage yield of oil which can be easily recovered from seeds at low cost. Oil acreage productivity is a combination of two factors: seed oil content and seed acreage yield. Oil content of different seeds investigated in this study ranges from 25% to 32% as shown in (Table 3); croton seed have the highest oil production and AJF yield potential (10 Mg ha^{-1} year^{-1} and 2400 L ha^{-1}, respectively).

Screening candidate bioenergy feedstock plants for invasiveness is receiving increased scrutiny.[218,219] The invasiveness risk (yes or no) of candidates is reported in Table 3 as determined by the Hawai'i-Pacific Weed Risk Assessment (HPWRA) (2012) and other references. Croton, jatropha, banagrass, blue gum eucalyptus, rose gum eucalyptus, and saligna eucalyptus were considered as invasive (high risk) species, while gliricidia, kamani, sesbania, hybrid leucaena, rainbow eucalyptus, robusta eucalyptus, rice, and sorghum were considered not invasive (low risk) species. Pongamia invasiveness status is listed as yes and no; it is considered to not be an immediate problem in the tropics according to Binggeli et al.,[72] while HPWRA considered it high risk. The invasive status of energycane is also unclear (yes and no, Table 3) because it is a hybrid, and its invasiveness depends on the parental variety and genotype as

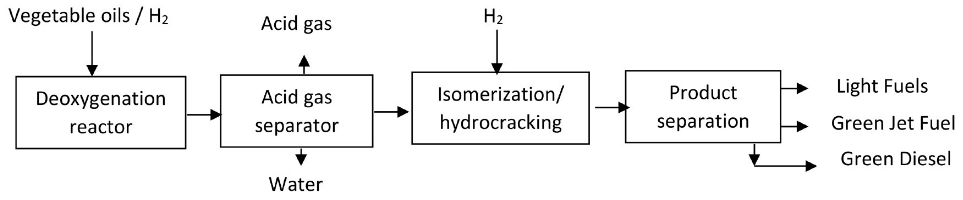


Figure 14. Simplified schematic of UOP's Renewable Jet Fuel process. Adapted from *Renewable and Sustainable Energy Reviews*, Vol. 25, Liu, G.; Yan, B.; Chen, G. Technical review on jet fuel production, 59−70 (ref 228), Copyright 2013, with permission from Elsevier.

well as environment interactions.[220] Therefore, invasive risk must be assessed for each individual clone and environment.

Further research is required to widen the database on alternative species for bioenergy production. In particular, there is a need to evaluate fiber species that have high wood density and high to moderate volume growth rates.

3. CONVERSION OF BIOMASS TO ALTERNATIVE JET FUEL (AJF)

In this section, information from the literature regarding the conversion of the crops discussed in this review to AJF are summarized. An overview of the current state of development for six biomass to jet fuel conversion processes is provided, gasification-FT (FT), fast pyrolysis (PY), hydrothermal liquefaction (HTL), direct sugars to hydrocarbons (DSCH), alcohol to jet (ATJ), and hydrotreated esters and fatty acids (HEFA). With regard to the DSCH and ATJ processes, the focus was placed on the production of sugars via hydrolysis of lignocellulosic biomass and the production of alcohols by methods other than fermentation of sugars. Where possible, mass and energy balances are provided for each process as well as estimates of capital and production costs.

The main focus of the report is the conversion of tropical biomass species to chemical compounds with carbon numbers in the jet fuel range, C_{10} to C_{16}. In almost all cases, however, there is insufficient information available to determine mass and energy balances or costs for the feedstocks of interest. In these cases, data for nontropical biomass species are used.

A thorough review of the literature is provided for the processing of the 17 crops discussed in this manuscript by appropriate conversion technologies. Only five of the crops examined in this report have been widely studied; these are sugarcane bagasse, rice straw, rice husks, jatropha, and pongamia. A summary of the stage of development each feedstock-technology combination has reached is provided in Table 45. This review does not include analysis to identify opportunities for overall process improvements that might be gained by integrating multiple feedstocks under one biorefinery operation.[222] While important, this lies outside the scope of this work.

3.1. Oil Crop Conversion.

Hydrotreated renewable jet (HRJ) is produced from fatty acid triglycerides from oil feedstocks (vegetable oils, waste cooking oils, seed oils, tallow, etc.) where free fatty acids (FFA) are typically generated via propane cleavage.[223,224] A number of useful reviews on this technology can be found elsewhere.[225−229] Other processes for the conversion of vegetable oils into jet fuels include hydrolysis, decarboxylation, and reforming;[230] these additional processes are *not* discussed further in this review.

A summary of the oil yield for each of the oil crops studied in this review is provided in section 2.3. A summary of fatty acid profiles of oils recovered from the seeds of jatropha, croton, pongamia, and kamani are presented in Supporting Information Section S1 and Tables S1.8−S1.11, respectively.

Oil feedstocks can be converted to jet fuel range hydrocarbons (HRJ) using traditional refinery operations for hydrotreating, hydro-deoxygenation, hydro-cracking, isomerization, and nitrogen, sulfur and metals removal. The product from these combined processes is often referred to as 'hydro-treated renewable jet (HRJ)' or 'hydro-treated esters and fatty acids (HEFA)'.[223,231] HRJ has been ASTM approved for blending at levels up to 50% with conventional jet fuel.[223] To date (2016) thousands of gallons of HRJ have been commercially produced.[232] A typical HRJ process flow diagram has been reported by Wang & Tao.[223] The process consists of four main steps (deoxygenation, gas separation, isomerization/hydrocracking, and products separation), a simplified example is provided below in Figure 14, based upon UOP's renewable jet fuel process.[233] This technology is currently employed by AltAir and Neste Oil.

It should be noted that HRJ/HEFA is a different process to biodiesel production that converts fatty acids in triglycerides to fatty acid methyl esters (FAME) via trans-esterification. FAME's are not suitable for use as jet fuel on their own, although they may be blended with conventional jet fuel at ratio of 20−30%.[234,235] Other issues for FAME's are poor storage stability, poor cold flow properties and engine incompatibility.[236,237]

All the process steps required to produce HRJ are commercial practices, therefore the technological aspects will not be reviewed herein. The main hurdle to the widespread production of HRJ is the availability of the oil feedstock at a price that makes the process economically viable. For background information on technological aspects of HRJ/HEFA process routes refer to the following publications.[223,231,232,236,238] Detailed compositions of HRJ/HEFA fuels derived from beef tallow, poultry fat, waste greases, and camelina (*Camelina sativa*) oil were reported by Corporan et al.[239]

The feedstock costs of some common oils has been reported by Wang & Tao[223] (2016) including jatropha 0.50 \$/kg, palm 0.79 \$/kg, camelina 1.75 \$/kg, algae 3.55 \$/kg, waste cooking oil 0.12−0.47 \$/kg, soybean 1.14 \$/kg, rapeseed 1.72 \$/kg and biomass pyrolysis oil 0.26 \$/kg. Note, pyrolysis oil is not a triglyceride (it is provided for comparison).

HRJ Mass Balances: Wang and Tao[223] summarized the production yields of intermediates and HRJ for eight feedstocks normalized to "gallons of gasoline equivalent" (GGE) product per dry Mg of feedstock, as of 2016. Feedstock is defined as the unprocessed oil seed or the oil after extraction. The intermediate yields range from ∼50 to 128 GGE/dry Mg with soybean having the lowest yield and rapeseed having the greatest. In terms of HRJ yields the range is 34 to 85 GGE/dry Mg (30 to 75 gal/dry Mg).

For Jatropha seed with 35% oil content, the intermediate yield is 92 GGE/dry Mg which equates to ~68 GGE HRJ/dry Mg (~60 gal/dry Mg).[223] For further detail on Jatropha see sections 2.1.1 and.3.1.1

Production costs: There is limited information in the open literature for production, capital and operating costs of HRJ/HEFA processes. The following is a summary of the findings from a 2016 review article.[223] The minimum selling price (MSP) of HRJ produced at a facility with capacity of 98 MM gal/year was $4.1/gal ($3.6/GGE, 2011 US$ basis). At a smaller scale of 30 MM gal/year the MSP increased to $4.8/gal. Both MSP's were based on using soybean oil as feedstock at a cost of 2.65 $/gal.[223,226] Maximizing jet fuel yield would require additional hydrogen that would add an extra ~ $0.30/gal to the MSP.[223] Based on a range of different feedstocks, the production cost of HRJ ranges from 4.1 to 9.2 $/gal where soybean and algae represent the lowest and highest production costs, respectively.[223] Pongamia oil derived HRJ has been estimated to cost $8.9/gal (2011 US$);[223,240] further results for pongamia oil are discussed in Section 3.1.4 below.

Wang and Tao[223] also estimated that HRJ capital costs are ~20% greater than biodiesel production (FAME) due to the hydro-treating required by the HRJ process. Although more costly, the coproducts from HRJ processes (hydrocarbons) have greater value than the glycerol byproduct from the FAME process. Feedstock cost is the greatest contributor to MSP, accounting for 70−80% of costs. There are relatively few studies reported for HRJ production using tropical oil crops. Most of the publications identified only consider the production of biodiesel (FAME).

Strengths and Weaknesses of HRJ: The main strengths and weaknesses of HRJ/HEFA processes routes are summarized in Table 4. One of the main disadvantages is that HRJ methods do not produce aromatics which comprise 10−25 wt % of conventional jet fuel.[241]

Table 4. Summary of the Strengths and Weaknesses of HRJ/HEFA Processes

strengths	weaknesses
• mature technology	• cost of the feedstock
• uses exiting refinery practices	• limited availability of feedstocks
• high-energy density product	• Aromatics are not produced.
• The product is free from the "blend wall" limitations imposed on bioethanol and biodiesel (FAME).	

3.1.1. *Jatropha Conversion.*

Most of the published studies on jatropha are focused on developing plant genetics to improve seed oil yields, or related to the production of biodiesel (FAME). Below is a summary of all the publications that are related to the production or testing of HRJ/HEFA derived from jatropha oil as well as some relevant studies on the use of jatropha derived FAME.

Wang and Tao[223] estimated that the yield of intermediate product from the conversion of jatropha to HRJ as ~92 GGE/dry Mg feedstock, with a HRJ yield of ~68 GGE/dry Mg (60 gal/dry Mg), based on the jatropha seed containing 35% raw oil.

Sivakumar et al.[232] evaluated spray characteristics of jatropha derived jet fuel under conditions representative of a jet engine. Blends of jatropha HRJ and jet fuel A-1 of 20:80 and 70:30 were tested and compared to pure jet fuel A-1. The fuel properties of the three samples were provided. The authors concluded that the jatropha HRJ/A-1 blends performed equally well as pure jet fuel A-1, confirming its suitability as a drop-in replacement for conventional jet fuels. A number of other studies of fuels properties of pure jatropha oil and it is methyl ester have been reported, mainly focused on comparisons to diesel fuel, see references cited in[232] for details.

Badmi et al.[235] studied the performance of a blend of jatropha methyl ester oil (FAME - 30%) and jet fuel A-1 (70%) in a small turbo jet engine. A 25−30% reduction in unconverted hydrocarbon emissions was observed for the blend compared to pure jet fuel A-1.

Bailis and Baka[31] reported a LCA and GHG emission study for jatropha HRJ produced in Brazil, including the effect of land use changes. The data for jatropha was based on surveys of Brazilian farmers and processors. The mass balance for HRJ for jatropha reported that 177 kg of dry fruit (seeds and husks) produced 46.7 kg semirefined oil that yielded 22.6 kg of HRJ equal to 1 GJ of energy. Based on a dry fruit yield of 4 tons per hectare per year, the use of drip irrigation and an assumed 20 year plantation lifetime with no direct land use changes, the GHG emission where ~55% lower than for conventional jet fuel. However, the GHG emission vary significantly depending on land use changes, in the best case an 85% reduction could be achieved but in the worst case, a 60% increase resulted.

As of 2010 Brazil has over 40 000 ha of jatropha cultivation with significant crop development undertaken by the federal agricultural support and support organization (EMBRAPA).[31] The authors point out that although jatropha is typically considered to thrive in poor quality land and require few inputs (irrigation, fertilizer), this is rarely the case in practice (i.e., jatropha does not thrive under such conditions).

Kumar et al.[224] developed a series of catalysts for hydroprocessing neat jatropha oil and its mixtures with conventional gas oil (a heavy petroleum fraction, typically the fraction between kerosene and lubricating oil). The aim was to find a catalyst that was insensitive to the FFA content of the jatropha oil which can vary from 1 to 25% depending on the source, had highly selectivity for diesel and was recyclable. The potential for coprocessing with petroleum derived gas oil was also examined. As the focus of the study was on the production of diesel range alkanes it is not discussed further.

Baroutian et al.[234] developed a two-step catalytic process for converting jatropha and waste cooking oil into methyl esters (FAME). The production of methyl esters from oil crops is less complex and is expected to be more cost-effective than hydroprocessing to produce HRJ which requires high temperatures (~300 °C) and elevated pressure (~80 bar). Trans-esterification also uses cheaper catalysts and has short reaction times than hydroprocessing. A two-step process is preferable due to the high FFA concentration in jatropha and waste cooking oil which forms fatty acid salts (soap) in an alkali trans-esterification process. Soap is difficult to separate from the methyl esters. The first process step used acid catalyzed esterification and the second step used base catalyzed esterification. The methyl esters produced from jatropha and waste cooking oil were blended in various ratios with conventional jet fuel A-1 and their ability to meet jet fuel specifications was determined. It was found that blends containing up to 20% methyl esters could be used without significantly changing fuel properties, although it is unclear whether the full sets of tests were applied. It should be noted that such blends are not qualified for use in jets at this time.

Verma et al.[236] developed two nickel based catalysts and studied their effectiveness for the production of alkane and aromatic compounds in the diesel and jet fuel range from jatropha oil using a catalytic hydrothermolysis process. The effect of reaction temperature and pressures was examined using a bench scale fixed bed reactor (single stage process). Liquid hydrocarbon yields of up to 84 wt % were achieved with a product distribution of ∼40% diesel range, 40% jet fuel range, and 20% gasoline range. The jet fuel fraction also contained ∼8% aromatics and had a similar freezing point as conventional jet fuel A-1. According to the author this is the first single stage process for the production of HRJ with the added benefit that aromatics are also produced, which is not the case with current two-stage process routes.

Jatropha is being cultivated in over 50 countries with over 1 million ha in production, as of 2008.[31] Test flights using blends of HRJ from jatropha and conventional jet fuel have been reported.[31] Mezher et al.[241] studied the risk of environmental contamination from jatropha derived HRJ and found that HRJ has lower toxicity than conventional jet-A fuel.

3.1.2. Kamani Conversion. No publications on the production of HRJ/HEFA from kamani oil were identified. Only a couple of papers on the oil content of kamani kernels and one related to biodiesel were identified; summaries of those studies are provided below.

The kernels from kamani have up to 75% oil content (dry basis), the oil contains ∼70% unsaturated fatty acids (mostly oleic and linoloeic acids).[242] Islam et al.[243] studied kamani (*Calophyllum inophyllum*) oil extraction methods. The greatest oil yield was 40−50 wt % of the kernel when using hexane extraction.

Putri and Gheewala[209] reported an energy analysis for biodiesel production from kamani oil via trans-esterification. The analysis showed that the process consumes less energy than contained in the biodiesel produced, meaning it is suitable for use as a renewable energy source.

3.1.3. Croton (Musine) Conversion. No publications were identified for biodiesel (FAME) or HRJ/HEFA production from this feedstock.

3.1.4. Pongamia (Karanja Oil) Conversion. There are a large numbers of publications on pongamia oil (>300); however, most of the articles are related to the production of biodiesel or direct combustion of the oil. Some of the more relevant publications are described below.

The kernel from pongamia contains ∼10 wt % moisture and ∼30−40 wt % oil, which is primarily composed of eight fatty acids;[78,238] refer to the publications and references therein for further details of the raw oil properties. Pongamia is being grown for oil production in a number of countries including USA, India, Japan, China, Australia, and Malaysia.[78]

Jaya et al.[238] studied the trans-esterification of pongamia oil using heterogeneous ion-exchange resin catalyst for production of biodiesel. This is due to concerns over the cost of using strong acids and bases as catalyst in conventional biodiesel production and the difficulty of recovering the methyl esters from the reaction mixture. As the focus of the cited study is on biodiesel production, it will not be discussed further.

Klein-Marcuschamer et al.[240] made an open source model for the techno-economic assessment (TEA) of the production of HRJ from pongamia oil, microalgae, and sugarcane molasses. Detailed process flow diagrams for the processes were presented. Pongamia oil was assumed to be recovered by hexane extraction, based on data from soybean processing with oil recovery of 96%, followed by degumming and refining of the triglyceride mixture using UOP's Ecofining process to produce HRJ. A similar process was used for microalgae. For molasses, a fermentation based approach was assumed where sucrose was converted to farnesene using an engineered yeast (based on Amyris's process), followed by hydro-cracking and isomerization to produce HRJ. The analysis suggests that HRJ from pongamia, microalgae, and molasses was competitive with conventional jet fuel when the cost of a barrel of crude oil exceeded \$374, \$1343, and \$301, respectively.

Ortiz-Martinez et al.[78] examined trans-esterification of pongamia oil via a catalyst free one-step method using supercritical methanol to produce biodiesel. Refer to the publication for further details and to references therein for details regarding the conventional two-stage conversion of pongamia oil to biodiesel.

Verma and Sharma[244] compared and optimized the use of methanol and ethanol in the production of biodiesel via trans-esterification of pongamia oil. This was to overcome the complications related to the high concentration of FFAs in pongamia oil and other vegetable oils which cause problems due to soap formation. See citations therein regarding the aspects of pongamia oil derived biodiesel that have been studied to date (2016). The authors note that relatively few studies have been performed compared to other feedstocks.

Parida et al.[245] used an ultrasound-assisted method for the rapid production of biodiesel (FAME) from mixtures of karanj (pongamia) and soybean oil. Refer to the publication for further details. Anjana et al.[246] developed heterogeneous catalysts for the trans-esterification of pongamia oil using methanol and tested the biodiesel produced in a diesel engine. Rao et al.[247] tested a two-step catalytic trans-esterification process for the production of biodiesel from pongamia oil, using acid catalyst followed by alkaline catalyst.

Dwivedi and Sharma[248] have studied the oxidation stability of pongamia derived biodiesel. Bobade and Khyade[75] examined the properties of pongamia oil in relation to the production of biodiesel. Avulapati and Ravikrishna[249] studied the atomization and spray characteristics of pure jatropha and pongamia oils in relation to direct injection in to a diesel engine.

3.2. Fiber Crop Conversion. Tropical fiber crops include soft and hard woods, grasses (herbaceous biomass), and agricultural residues (sugarcane bagasse, rice husks, and rice straw). Thermochemical processes (FT, PY, or HTL) are well suited to the production of jet fuel from these feedstocks; these methods are described and discussed in this section. An alternative pathway to jet fuel from fiber crops is through the production of sugars and/or alcohols intermediates, and these approaches are discussed in sections 3.2.4 and 3.2.5.

3.2.1. Gasification-FT. Biomass gasification can be performed in a number of different ways, with various reactor configurations (fluidized bed, entrained flow, circulating beds, fixed bed, moving bed, updraft, or downdraft) and using different gasification mediums (air, steam, oxygen, or combinations of the aforementioned). Gasification processes can also be designed to operate at different pressure and temperatures and with different approaches for downstream processes to manage tar and remove other species (contaminants) that cause deposition problems or poison catalysts (typically S, Cl, K, and NH_4).[7,250]

Gasification is an endothermic process, requiring supplemental thermal energy to drive the reactions. Autothermal gasifiers generate heat by partial feedstock combustion while allothermal gasifiers use an external heat source. In addition to the various ways gasification can be performed, there are two main options for converting producer gas to liquid fuels, Fischer−Tropsch (FT) synthesis or fermentation.[223,251]

FT synthesis was developed in the 1920s as a way of converting mainly CO/H_2 mixtures (producer gas or synthesis gas or "syngas" when it is used in FT processes) into hydrocarbons ranging from gases to heavy waxes. The term producer gas is used in this report. The process is typically catalyzed with metals (most commonly Fe or Co).[252] FT synthesis is most often used to produce liquid hydrocarbons (gasoline to diesel) from coal derived producer gas or from reformed natural gas; more recently there has been growing interest in the use of biomass feedstocks, and in the production of alcohols (primarily methanol, ethanol, or butanol).[252] A couple of reviews on the FT synthesis of alternative jet fuels are also available.[228,229]

The gasification-FT process can be broken down into four main process steps: (1) biomass pretreatment (particle size reduction, drying, leaching/washing), (2) gasification and gas cleanup, (3) FT-synthesis, and (4) upgrading to produce high-quality fuels.

To date there are no full scale commercial gasification-FT plants operating with biomass feedstocks, although there are a number of plants operating at demonstration scale (i.e., the Gussing facility in Austria). The main problem encountered when using biomass as feedstock for gasification-FT is the lack of homogeneity of the feedstock (i.e., inconsistent water content, density, particle size, and energy content), which makes it difficult to maintain consistent conditions in the reaction chamber unless a single biomass type is used.[252] The high moisture and oxygen contents of biomass lead to low heating values of the producer gas and often lead to greater production of CH_4 than desired and less H_2. The ideal H_2/CO ratio of the producer gas for FT synthesis of liquid fuels is 2:1.[165]

There are three main types of gasifier suitable for processing biomass (1) fixed-bed or moving bed designs, (2) fluidized-bed, and (3) entrained flow configurations. A brief description of each reactor system is provided in Supporting Information Section S2 along with information on FT conversion pathways for liquid fuel production and methods for contaminants removal.

3.2.1.1. Economics, Mass, and Energy Balances (FT). Coal gasification technology has been widely applied in the chemical industry to produce town gas and hydrogen and coupled with chemical synthesis to produce chemical intermediates, fertilizers (e.g., ammonia and urea), and liquid fuels (gasoline to diesel).[253] It is anticipated that experience gained from coal operations can be transferred to solve problems related to biomass. However, some technical barriers related to biomass gasification-FT still require further study.

FT synthesis for liquid fuels and chemicals based on the gasification platform is technically feasible. Many coal-to-chemicals processes have integrated gasification, gas cleaning, reforming, and synthesis. System economics are mainly related to availability, supply, and cost of feedstock as well as the scale of the facility. These variables lead to a number of possible process configurations and the selection of technology often depends on the scale. Compared to fossil fuels, the biomass supply and transportation are a challenge. To avoid this problem and improve economic feasibility, it is important to size facilities to match the local biomass resources and/or to produce intermediate products from the biomass (such as bio-oil), which can be transported over greater distances more economically to a centralized facility for upgrading to FT-liquids.[253] Furthermore, the competitiveness of future biomass FT production strongly depends on the evolution of a biomass market as well as ongoing technology development and optimization of system configurations.

A wide range of scales is reported for FT synthesis plants[253] and generally, larger scale plants are more economical. The Shell GTL (Gas to Liquid) plant in Malaysia (1993) produced liquid fuels at 12 500 bbl (barrels) per day (i.e., ~1000 MW_{th} fuel input−natural gas), while a newer plant in Qatar has a capacity 6 times higher with 75 000 bbl per day of liquid fuels production (~6000 MW_{th} as fuel input−natural gas). A plant size of ~1000 MW_{th} is typical and would require about 5000 Mg of dry biomass per day. However, a smaller scale FT plant (100−200 MW_{th} biomass input), cited by Hamelinck et al. in 2004,[254] indicates that FT diesel could be competitive with fossil diesel with a tax exemption, as is the case in Europe.

Production of FT-liquids: Tijmensen[255] estimated the cost for a 367 MW_{th} fuel input FT synthesis plant in 2002 to be in the range of $280−450 million. Similar results were reported by Hamelinck et al.,[254] who estimated the total capital investment cost of a similar scale plant (400 MW_{th} fuel input) to be €286 million in 2004. Hamelinck's plant included a 25 bar oxygen-blown gasifier, a tar cracker, wet gas cleaning, and a solid bed FT reactor with 70% conversion in once-through conversion mode. In such a configuration, the overall efficiencies (energy in the liquid fuel products divided by the energy in the biomass fuel) for the best configuration were 40−45% on a higher heating value (HHV) basis. Production cost of FT liquids were estimated as 16 €/GJ or 2.45 €/Gal ($2.16/Gal in 2002). Table 5 summarizes the influence of scale on the costs of investment and FT fuel products based on the plants with 80, 400, 1000, and 2000 MW_{th} fuel input.[254]

A techno-economic analysis report from NREL by Swanson et al.[256] presents the recent (2010) state of biomass FT synthesis. The report compares the capital and production

Table 5. FT Synthesis Plant Scale and Relevant Cost Estimates[a]

capacity, MW_{th}	fuel input, Mg/day	FT fuel output, bbl/day	investment cost, €, million	FT fuel cost, €/gal
80	384	454	90	3.5
400	1 920	2 270	286	2.5
1 000	4 800	5 676	625	2.2
2 000	9 600	11 351	1 100	2.1

[a] Reprinted from *Energy*, Vol. 29 (11), Hamelinck, C. N.; Faaij, A. P. C.; den Uil, H.; Boerrigter, H., Production of FT transportation fuels from biomass; technical options, process analysis and optimization, and development potential. pp 1743−1771. Copyright 2004, with permission from Elsevier (ref 254). Assumptions and calculations: 1. €1 = $0.88 in 2002. 2. HHV = 152 MJ per gal of FT product. 3. For a FT synthesis plant, a capacity of 740 MW_{th} (HHV) input is equivalent to 10 000 bbl/day (420 000 gal/day) output of FT products. 4. HHV of biomass is assumed as 18 MJ/kg on dry basis; 1 MW_{th} = 86 400 MJ/day, then input (kg/day) per MW_{th} capacity = 86 400 (MJ/day)/18 (MJ/kg) = 4.8 Mg/MW_{th}. 5. For 400 MW_{th} input FT plant: biomass input = 4.8 Mg/day/MW_{th} (400 MW_{th}) = 1 920 Mg/day.

costs for two temperature scenarios, low temperature (LT) scenario and high temperature (HT) scenario, based on a gasification platform with a 2000 Mg/d corn stover feed rate. The gasifier selected in the LT scenario was an oxygen blown, low-temperature (870 °C), nonslagging, fluidized bed gasifier. The HT scenario is based on an oxygen blown, high-temperature (1 300 °C), slagging, entrained flow gasifier. The producer gas from the gasifier is used for FT synthesis, hydroprocessing, and electricity production in both scenarios. The energy balance and mass flow rates are listed in Table 6.

Table 6. Overall Mass Flow and Energy Balance in the Scenarios of Biomass-to-Fuels Based on Gasification[a]

	HT scenario	LT scenario
input, Mg/day	2 000	2 000
output, electricity net export, MW	13.82	16.36
output, gallon gasoline equivalent, GGE	122 000	94 400
efficiency, %, excluding electricity, on LHV basis	50	39
efficiency, %, Including electricity, on LHV basis	53	43
capital cost, M$	610	500

[a] Reprinted from *Fuel*, Vol. 89, Swanson, R. M.; Satrio, J. A.; Brown, R. C.; Platon, A.; Hsu, D. D. Techno-economic analysis of biomass-to-liquids production based on gasification. pp S11−S89, Copyright 2010, with permission from Elsevier (ref 256).

The total capital investment required for the *n*th plant scenarios has been reported as $610 million for the HT scenario and $500 million for the LT scenarios.[256] The product value for the HT and LT scenarios are estimated to be $4.30 and $4.80 per GGE, respectively, based on a feedstock cost of $82 per dry Mg.

Cost analyses from various sources are summarized in Table 7. It can be concluded that cost estimates vary greatly depending on the underlying assumptions, the level of technological development, and plant size.[256] However, the product value seems to fall into a relatively narrow range of 12−16 $/GJ.

Table 7. Comparison of Techno-Economic Studies of Biofuel Production Plants Based on Biomass Gasification

	Williams et al.[257]	Phillips et al.[258]	Tijmensen et al.[255]	Larson et al.[259]
cost year	1991	2005	2000	2003
plant size (dry metric ton per day)	1 650	2 000	1 741	4 540
feedstock	generic biomass	poplar	poplar	switchgrass
fuel output	methanol	ethanol	FT liquids	diesel, gasoline
feedstock cost ($/dry short ton)	41	35	33	46
capital investment ($MM)	N/A	191	387	541
product value ($/GJ)	15	12	16	15
product value ($/GGE)	1.90	1.60	2.00	1.85

Cost Estimation for Fuel Ethanol Synthesis: He et al.[260] performed an economic analysis for a biomass ethanol synthesis plant (2011). The total capital investment cost of the 370 MW_{th} plant was estimated to be about €100 million, and the ethanol production cost was about 0.25 €/L. Additionally, ethanol production cost decreased with increasing plant scale.[260]

The capital investment in a biomass ethanol synthesis plant can be broken down into pretreatment, gasification, gas cleaning (including tar/CH_4 reforming), alcohols synthesis, alcohols separation and purification, power generation, and utilities. The biggest share of capital investment was allocated to producer gas cleaning at ∼38%, followed by ∼16% for biomass pretreatment and ∼15% for alcohol synthesis. These costs scaled linearly with plant sizes ranging from 50 MW_{th} to 800 MW_{th} input.[260] Refer to the alcohol production section of this report for more details (section 3.2.5).

3.2.1.2. Summary of Gasification-FT. Based on the literature review provided in the previous sections, there are two general modes of gasification that are suited to the production of jet fuel from biomass: (i) steam blown, low to medium temperature, atmospheric pressure fluidized bed designs or (ii) oxygen blown, medium to high temperature, elevated pressure fluidized bed or entrained flow designs. An emerging approach is the use of mixtures of steam and oxygen to reduce the amount of oxygen and related costs; this mode of gasification in only touched upon briefly in this report due to a lack of information.

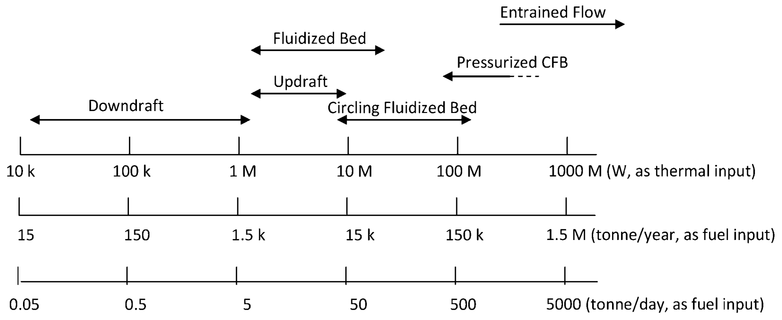
The most recent published study relevant to this discussion is a techno-economic analysis (TEA) by NREL and partners[261] from 2012. The conclusions from that study was that the most promising gasification-FT process route for biomass is steam blown, low pressure (33 psi), indirect dual-bed gasification (circulating entrained flow design). The biomass is gasified in a steam blown, circulating fluidized bed with the resulting char combusted in a second, air-blown, fluidized bed to heat the bed material (olivine/sand) that is circulated between the two reactors.

According to NREL's TEA, this approach is more cost-effective than oxygen-blown high temperature, pressurized, slagging gasification systems or lower temperature air blown gasification.[261] However, it should be noted that dual bed (circulating bed) biomass gasification reactors are more complex to operate and there is limited information on operating or maintenance costs due to limited experience at commercial scale (particularly for extended periods of operation). In the cited example, mixed alcohols were the primarily product,[261] but alternative jet fuel could be produced

Table 8. Typical Product Gas Composition (vol %) with Different Gasification Agents in Biomass Gasification[a]

heating source	gasification agent	H_2	CO	CH_4	CO_2	N_2
autothermal (directly heated)	air	11−16	13−18	2−6	12−16	45−60
	oxygen/steam (H_2O)	23−28	45−55	<1	10−15	<5
allothermal (indirectly heated)	steam (H_2O)	35−40	22−25	9−11	20−25	<1

[a] Reprinted with permission from Cui, H., Morgan, T. J., Petrik, T., Turn, S. Q. Report on Analysis of Integrated Tropical Biorefineries. Under Cooperative Agreement No. DE-FC26-06NT42847, Subtask 9.3 Deliverable. U.S. Department of Energy Office of Electricity Delivery and Energy Reliability, Hawai'i Natural Energy Institute: Honolulu, 2012 (ref 262). Copyright 2012 Hawai'i Natural Energy Institute.



Assumptions for calculation:

1. Biomass typical high heating value (HHV): 18 MJ/kg

2. Gasifier operation days per year: 80% of 365 days

Figure 15. Gasifier technologies vs scale (as fuel input). Adapted with permission from Bridgwater, A. V. The Future for Biomass Pyrolysis and Gasification: Status, Opportunities and Policies for Europe; Bio-Energy Research Group, Aston University (ref 263). Copyright 2002 European Commission.

Table 9. Summary of the Strengths and Weakness of Different Modes of Gasification

gasifier type	strengths	weaknesses
fixed-bed updraft	• feasible at small scale (<1.5 MW_{th}) • mature technology at small scale • high carbon conversion • can accept fuels with high moisture content • can accept fuels with high ash content	• requires fuel with a specific particle size range • high concentration of tar in product gas (100 g/Nm^3) • high concentration of particles in product gas • potential for slagging • medium thermal efficiency
fixed-bed downdraft	• feasible at small scale (<1.5 MW_{th}) • low concentration of tar in product gas (1 g/Nm^3) • low concentration of particles in product gas • produces a relatively clean product gas	• low thermal efficiency • requires fuel with low moisture content • requires fuel with low ash content
fluidized-bed	• can accept a wide variety of fuels • feasible at medium to large scale (5 to ~400 MW_{th}) • proven at commercial scale	• requires a fuel particle size <10 cm • medium amount of tar in product gas (~10 g/Nm^3) • bed agglomeration can be an issue
dual fluidized-bed	• nitrogen free product gas • can accept a wide variety of fuels • feasible at medium to large scale (5 to ~400 MW_{th}) • proven at commercial scale • producer gas has medium calorific value (~17−18 MJ/Nm^3) • high-energy conversion efficiency • good quality producer gas when steam blown (does not require pure oxygen)	• requires a fuel particle size <10 cm • medium amount of tar in product gas (~10 g/Nm^3) • bed agglomeration can be an issue • more complex to build than traditional fluidized bed and greater capital cost
entrained flow	• can accept liquid−solid fuel slurries • complete conversion of the fuel within a few seconds • very low levels of tar and methane in the producer gas • good quality producer gas which requires minimal gas cleaning • increased efficiency when used for synthesis • can accept fuels with ash that melts at low temperatures • proven at commercial scale (coal)	• requires a fuel particle size ~1 mm • requires pure oxygen • operates at high pressure (up to 100 bar) • operates at high temperature (~1200 °C) • greater capital costs than other gasifiers • requires large scale (~1000 MW_{th}) to be economically viable • limited experience with biomass feedstocks

by this approach after appropriate changes to the FT synthesis reaction conditions. The mass and energy balance for this process as well as costs are summarized in the alcohols section of this report (section 3.2.5).

Strengths and weakness of different modes of gasification: Table 8 lists the approximate gas composition from gasification of (generic) biomass via different modes of operation. Oxygen or steam blown gasifiers with indirect heating processes are preferred for liquid fuel or chemicals synthesis because the producer gas contains less nitrogen. Air-blown gasification is typically used to produce fuel gas for combustion for heat and/or power (electricity) generation.

There is an approximate relationship between the gasifier type and the scale that gives the lowest cost (economy of scale), as shown in Figure 15.[263] For a large scale application (up to hundreds MW_{th} fuel input), the preferred and most reliable system is the pressurized circulating fluidized bed (PCFB) gasifier or entrained flow gasifier. For small-scale applications (<10 MW_{th} fuel input), fixed bed gasifiers (updraft and downdraft) and bubbling fluidized-bed gasifiers are better suited. Circulating fluidized bed (CFB) gasifiers can be competitive in medium to large scale (10−100 MW_{th} fuel input) applications. Another option for a large scale application is to operate a group of small or medium scale gasifiers in parallel, e.g., Great Plains Synfuels Plant (North Dakota) ran 14 Lurgi gasifiers (fixed bed type) totaling 14 500 Mg/day (16 000 ton/day) of coal.[264]

In addition, pressurized gasification systems can increase the process capacity and energy efficiency compared with atmospheric systems. Based on an Aspen process evaluation, it has been reported that pressurized operation can increase the overall LHV (low heating value) energy efficiency by ~10%.[255] The main strengths and weaknesses of each mode of gasification that is potentially suitable for processing biomass are summarized in Table 9.

3.2.1.3. Gasification of Tropical Biomass Species. In all the studies cited in the previous gasification section, the feedstocks were mostly woody biomass or agricultural residues from temperate regions of North America or Europe. The gasification literature has been surveyed to assess the amount of information that is available for tropical feedstocks. Only studies on steam and/or oxygen blown gasification will be included, as air blown gasification generates a poor quality producer gas that is not suited to jet fuel production via FT synthesis.

Steam Blown, Indirectly Heated, Atmospheric Pressure, Fluidized Bed Gasification: Sugarcane Bagasse: In general terms, a steam blown, dual (circulating) fluidized beds, atmospheric pressure gasifier operating with bagasse as feedstock typically produces gas with a HHV of ~15 MJ/m^3 at a dry gas yield of ~0.75 m^3/kg dry bagasse (the gas composition was not reported).[265]

Researchers at HNEI have studied the steam gasification of bagasse obtained from the Gay & Robinson Sugar Factory on Kauai.[266] A lab-scale fluidized bed reactor (~1 kg/h feed rate) located at HNEI was used to perform the test. A gasification temperature of 850 °C was used with a steam to dry biomass ratio of ~0.6. The dry gas yield from the steam gasification of bagasse was ~1.1 m^3/kg dry fuel, on a N_2 free basis at STP.[266] The average product gas composition on a N_2-free, dry volumetric basis was 47.4% H_2, 24.5% CO, 8.8% CH_4, 18.8% CO_2, and 0.7% C_2H_4.

The concentration of sulfur species in the producer gas on a N_2-free, dry gas basis was ~100 ppmv H_2S, ~5 ppmv COS, and ~2 ppm of C_4H_4S.[266] Ammonia (NH_3), cyanide (HCN), and oxides of nitrogen (reported as NO) concentrations in the dry, N_2-free producer gas were on average ~1 850, ~23, ~19 ppmv, respectively. The concentration of tar in the producer gas on a N_2-free dry gas basis was ~26.5 g per m^3, benzene and naphthalene were the two dominant species in the tar accounting for 17.5 and 3.7 g per m^3.

In a separate study conducted at HNEI,[267] sugarcane bagasse and leucaena (grown in Hawai'i) were processed using the same a lab-scale steam gasification fluidized-bed reactor as used in the study mentioned above. The fate of metal elements (major and trace elements) as well as producer gas yield and composition obtained at 800 °C were reported.[267] Table 10 displays the operating parameters and the producer gas composition from these tests.

The results presented in Table 10 show that under equivalent conditions bagasse produces less gas than leucaena, ~3650 L/kg (dry basis, N_2 free) and ~7 000 L/kg, respectively. The ratio of H_2/CO is ~1.5:1 for bagasse and ~3.2:1 for leucaena. The ideal H_2/CO ratio for jet fuel production is ~2:1.

Ogi et al.[268] compared steam gasification and O_2-steam gasification of sugarcane bagasse and oil palm empty fruit bunches (EFB) using a lab-scale entrained flow reactor (100 cm high, 10 cm diameter). When using steam alone, carbon conversion into the gas phase was ~95% for EFB and ~90% for bagasse. The producer gas from EFB has a H_2/CO ratio ranging from 3.0:1 to 3.6:1, which is suitable for FT synthesis. The producer gas from bagasse under steam gasification conditions had a much lower H_2/CO ratio of ~1.5 to 1.8:1. When a mixture of O_2 and steam were used the carbon conversion increased to ~98% for both EFB and bagasse, with the H_2/CO ratio dropping to ~2.7:1 and to ~1.3:1 for EFB and bagasse, respectively.

Table 10. Average Operating Parameters and Gas Composition from Steam Gasification of Leucaena and Bagasse at Atmospheric Pressure[a]

parameter	bagasse	leucaena	leucaena (repeat)
temperature, °C	800	800	800
duration of run, h	5.13	6.65	6.85
fuel feeding rate, kg/h	1.11	1.17	0.96
fuel used, kg	5.68	7.42	6.60
steam rate, kg/h	1.97	1.99	1.84
product gas volume (dry basis, N_2 free), L	3654	7545	6488
Producer Gas Composition, N_2 Free, %			
H_2	40.7	48.9	48.0
CO	28.0	15.3	14.1
CH_4	11.5	9.0	7.8
CO_2	18.9	24.8	25.2
C_2H_4+	3.7	2.2	2.0
Sulfur Species in Dry Producer Gas, N_2 Free, ppm			
H_2S	156.8	98.6	103.4
COS	4.8	1.3	1.6
C_2H_4S	7.1	4.0	4.7
bed char, g	123	339	310
ash content in bed char, %	84.1	81.0	78.4
filter char, g	518	548	471
ash content in filter char, %	30.6	9.8	8.3

[a] Reprinted from *Fuel*, Vol. 108, Cui, H.; Turn, S. Q.; Keffer, V.; Evans, D.; Tran, T.; Foley, M., Study on the fate of metal elements from biomass in a bench-scale fluidized bed gasifier. pp 1−12, Copyright 2013, with permission from Elsevier (ref 267).

Leucaena: The fate of metal elements (major and trace elements) as well as producer gas yield and composition from steam gasification of leucaena (grown in Hawai'i) at 800 °C are summarized in Table 10.[267] The composition of the producer gas, tar yields and composition, sulfur compounds, and ammonia concentrations have also been reported from lab scale (~1 kg/h feed rate) steam gasification tests of leucaena (grown in HI) at ~800 °C.[269] The effect of two commercial nickel based and one zinc based catalyst on the above-mentioned properties was also studied,[269] Table 11 displays the producer gas composition before it passed through the catalytic bed.

The tar concentrations in the producer gas when no catalyst was used was ~15.5 g of GC-range tars per m^3 dry gas and ~5.3 g gravimetric tar per m^3 dry gas.[269] When the C11-NK nickel based catalyst was used, the GC-range tars were reduced to less than 0.1 g/m^3 dry gas and gravimetric tar to ~0.8 g/m^3. Another nickel based catalyst (G91) was less effective, reducing the GC-ranges tars to 1.0−2.5 g/m^3 dry gas and gravimetric tars to ~1.5 g/m^3 dry gas. Replacement of the catalysts with alumina silicate ceramic balls produced no

Table 11. Permanent Gas Composition in Product Gas Exiting the Hot Gas Filter (Before Passing through the Catalyst) by GC Analysis (vol %, Dry, N_2-Free Gas) from Steam Gasification of Leucaena[a]

	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6
average	51.9	12.7	6.9	27.4	1.0	0.07
standard deviation	3.3	1.0	0.8	2.2	0.3	0.05

[a] Reprinted from ref 269. Copyright 2010 American Chemical Society. The values are the average from 10 experiments.

significant reduction in the tar concentration, confirming that the tar reduction was the result of catalytic activity rather than thermal cracking.

The average concentration of sulfur species in the dry producer gas without ZnO sorbent were 93 ppm of H_2S, 2 ppm of COS, and 2 ppm of C_4H_4S (nitrogen free basis).[269] Including ZnO sorbent in the process reduced the sulfur species concentrations to ~0.1 ppm of H_2S and ~0.1 ppm of COS, while C_4H_4S concentration remained at ~2 ppm.

Although the fate of nitrogen compounds was not the main focus of the study, concentrations of NH_3 were measured with and without the presence of catalyst.[269] When no catalyst was used, the NH_3 concentration in the dry producer gas ranged from 2300 to 2700 ppm. G91 reduced NH_3 concentrations to 200 to 1100 ppm and C11-NK was more effective, lowering concentrations to less than 100 ppm.

Banagrass: No peer-reviewed publications on the steam gasification of banagrass were identified from the open literature. HNEI has conducted lab-scale steam gasification tests on banagrass, energycane, and leucaena to determine yields and compositions of the producer gas, tar, sulfur compounds, nitrogen compounds (ammonia, cyanide, and nitrogen oxides), chloride, and trace elements. This work is in preparation for publication (Cui and Turn - HNEI). The gasification tests were performed under the same conditions as previously reported for leucaena[269] as discussed above, and all the feedstocks were grown in Hawai'i.

The producer gas composition from G- and P-banagrass (green and purple banagrass), energycane, and leucaena are displayed in Table 12; the banagrass and energycane were pretreated before gasification.[270] The pretreatment method is described in Supporting Information Section S1. The fuel properties before and after pretreatment are also provide in Supporting Information Section S1. Briefly, the pretreatment steps in order of occurrence included particle size reduction using a shredder, dewatering via a screw press, rehydration with water, and a second dewatering. This process sequence is referred to as "S3" pretreatment.

The grass crops (G- and P- banagrass and energycane) generate a producer gas with similar composition and yield to one another, which is significantly different to that obtained for the woody biomass (leucaena) tested under the same conditions. The data in Table 12 shows that leucaena generates ~25% more producer gas than the grasses and the gas contains a greater proportion of hydrogen and less carbon monoxide. The ideal producer gas composition for FT synthesis of jet fuel is approximately 2:1 H_2/CO; leucaena has a H_2/CO ratio of ~4:1, while the grasses have a ratio of 1.6:1. The water−gas shift reaction (eq 1) can be used to adjust the gas composition and achieve the desired ratio of 2:1 H_2/CO as necessary.

$$H_2O + CO \leftrightarrow H_2 + CO_2 \qquad (1)$$

The concentration of nitrogen compounds in the product gas from the steam gasification of banagrass, energycane and leucaena (HNEI unpublished results) are presented in Table 13. Tables 14 and 15 display the corresponding results for HCl and sulfur compounds, respectively (HNEI unpublished results).

The results in Table 13 show that the producer gas from energycane and leucaena contain higher concentrations of nitrogen compounds (NH_3, HCN, and NO_x) than banagrass, totaling ~2900 ppm for energycane and leucaena (~2650 ppm of NH_3) and ~2000−2200 ppm for G-bana and P-bana, respectively (~1700−1900 ppm of NH_3). This accounts for 50−70% of the nitrogen in the feedstocks.

The concentration of HCl in the producer gas from G-bana, P-bana, and energycane are roughly equivalent considering the uncertainty in the measurements, containing ~60−140 ppm of HCl. No data is available for leucaena.

The total concentration of sulfur compounds in the producer gas was significantly higher for energycane (~240 ppm) than banagrass (~110−145 ppm) or leucaena (~100 ppm). The vast majority of the sulfur is in the form of H_2S (90−95%) for all the feedstocks. As part of the same unpublished study, the concentrations of major and trace elements in the dry producer gas were determined but are not discussed here.

Eucalyptus: Only one study was identified for the steam gasification of eucalyptus using a fluidized-bed reactor operating at atmospheric pressure. Franco et al.[271] examined the influence of feedstock (*Pinus pinaster*, *Eucalyptus globulus*, and *Quercus ilex*), temperature and steam to biomass ratio on the composition of the producer gas using a bench scale fluidized-bed reactor. The authors concluded that although the feedstocks generate slightly different producer gas compositions, the effect was minor in comparison to the influence of temperature and steam to biomass ratio. A temperature of ~830 °C and steam to biomass ratio of 0.6−0.7 w/w generated the greatest gas yields and hydrogen concentrations with the least tar, resulting in greater energy and carbon conversion than the other conditions tested.[271]

Table 12. Product Gas Composition (vol %) from the Steam Gasification of Banagrass (G, Green; P, Purple), Energycane, and Leucaena[a]

	volume %						yield
	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6	L/kg daf
G-banagrass S3	40.0 (2.7)	26.4 (2.5)	11.4 (0.9)	19.7 (1.1)	2.4 (0.2)	0.2 (0.0)	863 (35)
P-banagrass S3	39.6 (2.2)	25.1 (2.2)	11.6 (0.7)	21.2 (1.1)	2.3 (0.3)	0.3 (0.1)	887 (41)
energycane S3	40.5 (3.0)	22.9 (4.1)	11.3 (1.8)	22.9 (2.3)	2.2 (0.4)	0.2 (0.10)	814 (122)
leucaena	51.9 (2.3)	12.7 (1.3)	6.9 (0.6)	27.4 (1.2)	1.0 (0.4)	0.1 (0.0)	1136 (165)

[a] HNEI unpublished results. S3 refers to the sample having been pretreated. Standard deviations in parentheses.

Table 13. Gas Concentrations of NH_3, HCN, NO in Producer Gas and Their Fraction of the Fuel-Nitrogen (Fuel-N) from the Steam Gasification of Banagrass (G, Green; P, Purple), Energycane, and Leucaena[a]

	gas-N species, ppm			fraction of gaseous N species in fuel-N, %			
biomass	NH_3	HCN	NO	NH_3-N	HCN-N	NO-N	(NH_3, HCN, NO)-N
G-Bana S3	1700 (351)	304 (65)	–	46	8	–	54[b]
P-Bana S3	1891(17)	154 (26)	182 (21)	58	5	6	69
E-cane S3	2676 (29)	100 (32)	142 (44)	40	1	2	44
leucaena	2662 (484)	–	8.3[c]	61	–	0.2	61[d]

[a] HNEI unpublished results. S3 refers to the sample having been pretreated. Standard deviation in parentheses. –, data is unavailable. [b] Excluding NO-N. [c] Data from ref 269. [d] Excluding HCN-N.

Table 14. Gas Concentration of HCl in Producer Gas and the Fraction of the Fuel-Cl from the Steam Gasification of Banagrass (G, Green; P, Purple), Energycane, and Leucaena[a]

biomass	gas-Cl (as HCl), ppm	fraction of gas-Cl in fuel-Cl, %
G-Bana S3	141 (133)	28
P-Bana S3	62 (6)	11
E-cane S3	95 (41)	61
leucaena		

[a] HNEI unpublished results. S3 refers to the sample having been pretreated. Standard deviation in parentheses.

The experimental results reported by Franco et al.[271] are in good agreement with the findings from a theoretical study which compared energy and exergy analysis of eucalyptus, coconut shells, coir pith, and bamboo under steam gasification conditions.[272]

Many other studies on steam gasification of eucalyptus have been reported; however, those studies are not relevant to the present discussion as they were conducted using fixed bed reactors or were coprocessed with coal, or the gasification medium was a mixture of air-steam or oxygen-steam.

Rice Husks/Hulls: Karmakar and Datta[273] examined the effect of temperature and steam to biomass ratio on the production of a hydrogen rich producer gas from the gasification of rice husks in a lab-scale fluidize bed reactor that allowed the bed temperature to be controlled with external heaters. When operating at a bed temperature of 750 °C and a steam to biomass ratio of 1.0, the producer gas molar composition (dry basis) was 48.9% H_2, 22.7% CO, 22.2% CO_2, and 6.22% CH_4. A more detailed account of the findings at different temperatures and steam to biomass ratios is provided in Table 16.

The results in Table 16 show the expected trends where greater yields of H_2 and CO are achieved as temperature is increased while holding the steam to biomass ratio constant.[273] When the steam to biomass ratio is increased, the CO concentration decreases and H_2 yield increases (at constant temp.). The conditions that generate a producer gas that is suitable for FT synthesis of jet fuel are a gasification temperature of ∼750−770 °C and a steam to biomass ratio of ∼1.3. Under these conditions, a gas yield of ∼1.2 Nm^3/kg of raw rice husks (∼20 wt % ash) was achieved with a H_2/CO ratio of ∼3.0.

Loha et al.[274] studied the effect of temperature (650−800 °C) and steam to biomass ratio (S/B 0.75−2.00) on the composition of the producer gas from gasification of rice husks. The results (Table 17) are in close agreement with those reported by Karmakar and Datta.[273] A test conducted at 750−770 °C with a steam to biomass ratio of ∼1.3 generated a producer gas with a H_2/CO ratio of ∼3.0.[274] Loha et al.[274,275] also developed a model to predict the producer gas composition for rice husks, rice straw, and sugarcane bagasse. The results from the model indicate that under equivalent gasification conditions rice straw and bagasse have similar CO concentrations which are slightly lower than predictions for rice husks. H_2 yields are predicted to be greatest for rice straw and lowest for rice husks with bagasse showing intermediate behavior.

Rice Straw: Only one experimental study on the fluidized bed steam gasification of rice straw was identified. Xie et al.[276] examined the influence of calcium based catalysts (natural dolomite and limestone vs synthetic Ca-catalysts) on the steam gasification of rice straw using a circulating spout-fluid bed reactor. The optimum temperature for producing a good quality producer gas was ∼860 °C. The results obtained when using calcined limestone (CL), calcined dolomite (CD), and inert alumina (Al_2O_3) are summarized in Table 18. The results show that CL and CD improve the quality of the producer gas and increase the H_2 yield compared to alumina. CL and CD also reform some of the light hydrocarbons as they contain iron oxides. The H_2/CO ratio of the producer gas when using CL is ∼3.2, for CD ∼3.1 and for alumina ∼2.9.

Table 15. Gas Concentrations of H_2S, COS, and C_4H_4S in Producer Gas and Their Fractions of the Gas-S and Fuel-S from the Steam Gasification of Banagrass (G, Green; P, Purple), Energycane, and Leucaena[a]

	sulfur-containing species, ppm				fraction of sulfur species in Gas-S*, %			fraction of sulfur species in Fuel-S, %			
biomass	total	H_2S	COS	C_4H_4S	H_2S	COS	C_4H_4S	H_2S	COS	C_4H_4S	Gas-S
G-Bana S3	113 (12)	100 (9)	3 (1)	11 (3)	88	3	10	123	4	14	139
P-Bana S3	145 (21)	131 (18)	5 (1)	10 (2)	90	3	7	55	2	4	61
E-cane S3	243 (40)	227 (37)	6 (2)	10 (1)	93	2	4	53	1	2	57
leucaena	97 (14)	93 (14)	2 (0)	2 (1)	96	2	2	30	1	1	31

[a] HNEI unpublished results. S3 refers to the sample having been pretreated. Standard deviation in the parentheses. "Gas-S" includes H_2S, COS, and C_4H_4S.

Table 16. Carbon Balance and Gasification Efficiency of Experimental Results of Fluidized Bed Gasifier[a]

exp run no.	1	2	3	4	5	6	7	8
steam to biomass ratio	constant at 1.32				0.60	1.00	1.32	1.70
gasifier temperature (°C)	650	690	730	770	constant at 750			
Gas Composition (% mole)								
H_2	47.3	50.5	52.2	53.1	47.8	48.9	51.2	51.9
CO	11.3	12.8	15.9	17.9	27.5	22.7	19.7	17.4
CO_2	31.9	28.5	25.7	23.9	18.1	22.2	23.2	24.8
CH_4	9.6	8.16	6.3	5.2	6.6	6.2	6.0	5.9
HHV of prod. gas (MJ/Nm^3)	11.28	11.23	11.16	11.09	12.21	11.59	11.42	11.18
gas yield (Nm^3/kg of raw biomass)	1.03	1.12	1.16	1.21	1.05	1.09	1.16	1.21
carbon conversion (%)	84.10	85.82	85.83	87.88	84.83	86.25	87.68	90.11
cold gas efficiency (%)	62.99	64.78	65.58	66.06	65.75	65.96	66.10	66.15

[a] Reprinted from *Bioresource Technology*, Vol. 102, Karmakar, M. K.; Datta, A. B., Generation of hydrogen rich gas through fluidized bed gasification of biomass. pp 1907−1913, Copyright 2011, with permission from Elsevier (ref 273).

Table 17. Experimental Results from Steam Gasification of Rice Husks[a]

temperature (°C)	S/B	H_2 %	CO %	CO_2 %	CH_4 %
690	1.32	50.5	14.3	26.6	8.6
730	1.32	52.2	16.4	23.5	7.9
750	1.00	49.5	23.7	21.2	5.6
750	1.32	52.3	17.8	22.3	7.4
750	1.70	52.9	16.4	22.9	7.8
770	1.32	54.4	18.5	19.4	7.7

[a] Reprinted from *Energy Conversion and Management* Vol. 52, (3), Loha, C.; Chatterjee, P. K.; Chattopadhyay, H., Performance of fluidized bed steam gasification of biomass − Modeling and experiment. pp1583-1588, Copyright 2011, with permission from Elsevier (ref 274). S/B = steam to biomass.

Table 18. Gasification Results from Rice Straw with Various Bed Materials at 860 °C[a]

bed material	CL	CD	Al_2O_3
Gas Component (vol %, dry basis)			
H_2	52.3	51.5	48.9
CO	16.1	16.8	16.7
CO_2	25.1	24.6	26.8
CH_4	6.6	7.1	7.7
H_2 yield (mol/kg biomass)	29.4	29.2	22.8
tar yield (g/Nm^3)	4.6	3.7	8.9
carbon conversion (%)	91.4	94.0	82.0
total gas yield (Nm^3/kg biomass)	1.26	1.29	1.05

[a] Reprinted from ref 276. Copyright 2010 American Chemical Society. Calcined limestone (CL), calcined dolomite (CD).

Huijun et al.[277] performed steam-O_2 gasification of rice straw using a dual fluidized bed reactor. The aim of the study was to investigate a chemical looping method where an oxygen carrier (NiO/Al_2O_3) was used instead of molecular oxygen from the air. Optimized conditions, 750 °C with a steam to biomass ratio of 1.2 in the presence of a CaO-NiO oxygen carrier, yielded a volumetric gas composition of ~43% H_2 and ~28% CO with a producer gas yield of ~0.45 Nm^3/kg. Without the oxygen carrier, the producer gas yield was slightly lower (~0.38 Nm^3/kg) and the concentrations of carbon dioxide and carbon monoxide were slightly higher with a somewhat lower hydrogen concentration. This type of gasification process is still at the research stage of development.

Energycane: No publications were identified for the steam gasification of energycane. HNEI has conducted lab-scale steam gasification tests on energycane, banagrass, and leucaena to determine yields and compositions of the producer gas, tar, sulfur compounds, nitrogen compounds, chloride, and trace elements. This work is in preparation for publication (Cui and Turn, HNEI). The results are shown in Tables 12−15.

Sorghum: Only one publication was identified for the steam gasification of sorghum using a fluidized bed reactor. However, the focus of the paper was the mathematical modeling of fluid dynamics, heat transfer, and reaction kinetics under steam-O_2 conditions.[278] In addition, the feedstock was distillers dried grain (DDG) from grain sorghum, a byproduct of ethanol production. According to the publication, a lab-scale fluidized bed reactor was used and the influence of temperature, steam to biomass ratio, and equivalence ratio (with added oxygen) were examined. Experimental results for the producer gas yield or composition were not reported. The outputs from the model focused on fluid dynamics, heat transfer, and reaction kinetics.[278]

***Sesbania* and Glyricidia (Gliricidia)**: No papers were identified

Oxygen Blown, Indirectly Heated, Atmospheric Pressure, Fluidized Bed Gasification: Leucaena: The fate of fuel bound nitrogen in leucaena (grown in HI) has been studied in a lab-scale (~1 kg/h feed rate) oxygen-blown fluidized bed gasifier over the temperature range of 750−900 °C at atmospheric pressure.[279] Note: in this work the nitrogen in air was replaced with argon (O_2 + Ar) so that fuel nitrogen could be studied. The major species in the producer gas have been reported from tests with an equivalence ratio (ER, air-to-fuel) of 0.25 as a function of temperature and at a temperature of 800 °C as a function of ER (0.15−0.35).[279] In this report, ER is defined as the air-to-fuel ratio.

The major gas species produced during the atmospheric pressure O_2-blown gasification of leucaena as a function of temperature at an equivalence ratio of 0.25 are shown in Figure 16. Corresponding N_2 and NH_3 concentrations and NO and HCN concentrations are presented in Figure 17 and Figure 18, respectively. Figure 19 displays the concentrations of the major gas species as a function of ER at 800 °C. Table 19 summarizes the fuel nitrogen results as a function of temperature at an ER of 0.25.

As part of the same study, saw dust, bagasse, and three banagrass samples (pretreated by different methods) were also examined at a single set of conditions (800 °C, ER 0.25). The fate of the nitrogen from these feedstocks is presented in Figures 18 and 19, for NH_3 and NO, respectively. Table 20

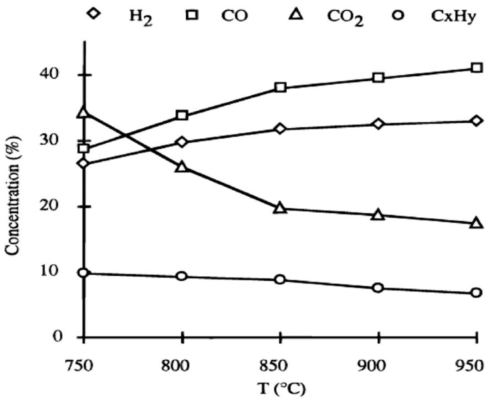


Figure 16. Major gas species composition vs temperature from oxygen gasification of leucaena (ER = 0.25). Reprinted from ref 279. Copyright 2000 American Chemical Society.

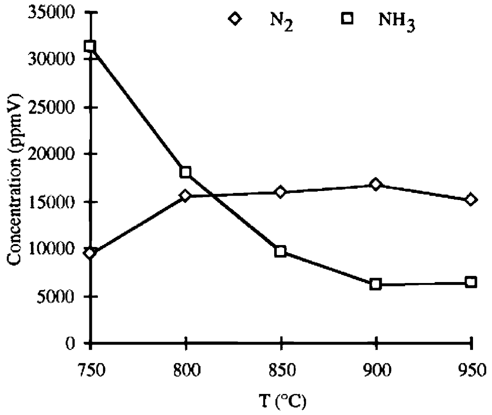


Figure 17. N_2 and NH_3 concentrations vs temperature from the oxygen gasification of leucaena (ER = 0.25). Reprinted from ref 279. Copyright 2000 American Chemical Society.

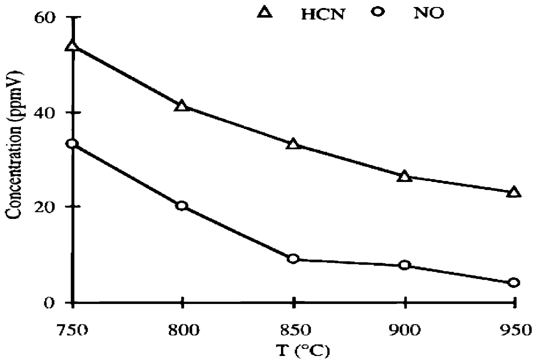


Figure 18. NO and HCN concentrations vs temperature from the oxygen gasification of leucaena (ER = 0.25). Reprinted from ref 279. Copyright 2000 American Chemical Society.

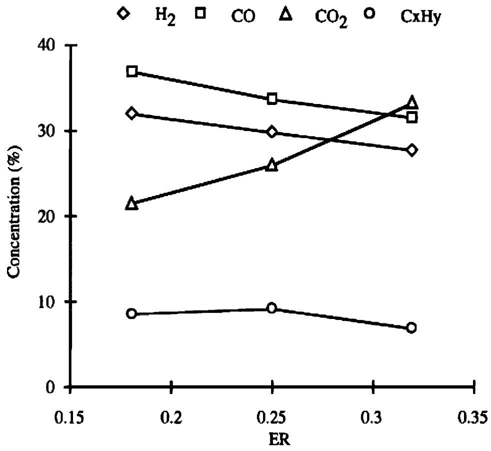


Figure 19. Major gas species composition vs ER from oxygen gasification of leucaena at 800 °C. Reprinted from ref 279. Copyright 2000 American Chemical Society.

Table 19. Distribution of Fuel Nitrogen As a Function of Temperature during Oxygen Gasification of Leucaena (ER = 0.25)[a]

	temperature (°C)				
	750	800	850	900	950
$N(NO_x)/N_{fuel}$, %	0.06	0.04	0.02	0.02	0.01
$N(NH_3)/N_{fuel}$, %	63.5	48.7	25.8	13.5	10.5
$N(HCN)/N_{fuel}$, %	0.11	0.09	0.08	0.07	0.07
$N(char)/N_{fuel}$, %	7.7	5.2	2.0	2.0	1.2
$N(N_2)/N_{fuel}$, %	38.6	69.9	80.3	88.7	85.7

[a] Reprinted from ref 279. Copyright 2000 American Chemical Society.

Table 20. NH_4^+ Nitrogen and NO_3^- Nitrogen in Feedstocks[a]

feedstock	$N(NH_4^+)$ ppmw	$N(NO_3^-)$ ppmw	$N(NO_3^-)/N(NH_4^+)$
sawdust	27.7	29.2	1.05
leucaena	214.9	41.0	0.19
bagasse	5.4	9.9	1.82
banagrass1	12.16	17.99	1.45
banagrass2	20.4	43.0	2.1
banagrass3	46.8	52.7	1.1

[a] Reprinted from ref 279. Copyright 2000 American Chemical Society.

provides information on the amount of NH_4 and NO_3 present in the feedstocks.

The concentration of NH_3 in the producer gas under oxygen-blown gasification conditions (Figure 20) follows the same trend as the amount of N in the feedstocks. Leucaena has the greatest concentration (~18 000 ppm of NH_3), followed by banagrass and bagasse (~4000–2000 ppm) with sawdust having the lowest concentration (~500 ppm). The amount of NO in the producer gas (Figure 21) is orders of magnitude lower than the NH_3 values and follow an inverse trend with sawdust having the greatest concentration (~110 ppm) and leucaena the lowest (20 ppm). These results correlate with the amounts and speciation (NH_4^+ or NO_3^-) of nitrogen in the feedstocks (Table 20).

Sugarcane Bagasse: The fate of fuel bound nitrogen for bagasse grown in Hawai'i has been studied using a lab-scale (~1 kg/h feed rate) oxygen-blown fluidized bed gasifier operating at atmospheric pressure, 800 °C with an ER = 0.25.[279] The composition and yield of the producer gas were not reported, and the results were shown in the previous subsection, Table 20 and Figures 18 and 19.

One other publication on the gasification of bagasse in the presence of oxygen has been published; however, the experiments were performed using an entrained flow reactor with a gasification medium composed of O_2 plus steam or with steam alone.[268] The findings from that study were summarized above in the steam gasification section.

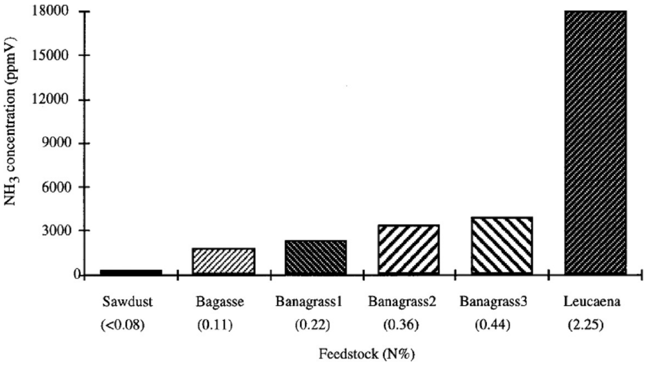


Figure 20. NH_3 concentration for sawdust, bagasse, leucaena, and banagrass under oxygen gasification at 800 °C and ER = 0.25. Three banagrass samples were tested, which had been prepared in different ways, banagrass1 = JC-PRP, banagrass2 = FC-PRP, banagrass3 = FC-P. Reprinted from ref 279. Copyright 2000 American Chemical Society.

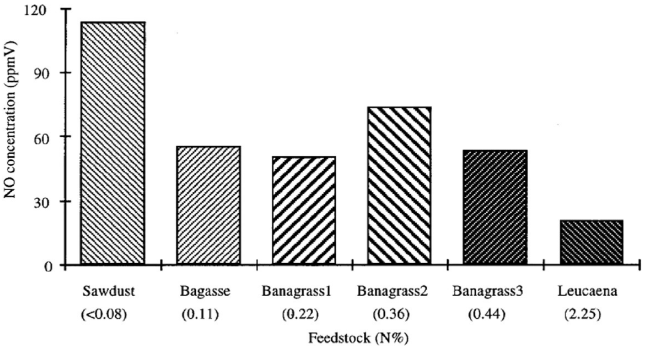


Figure 21. NO concentration for sawdust, bagasse, leucaena, and banagrass under oxygen gasification at 800 °C and ER = 0.25. Three banagrass samples were tested which had been prepared in different ways, banagrass1 = JC-PRP, banagrass2 = FC-PRP, banagrass3 = FC-P. Reprinted from ref 279. Copyright 2000 American Chemical Society.

Banagrass: The fate of fuel bound nitrogen has been studied in a lab scale (~1 kg/h feed rate) atmospheric pressure fluidized bed gasifier at 800 °C with an ER = 0.25 for banagrass (grown in HI) after 3 types of pretreatment (JC-PRP, FC-PRP, FC-P).[279] Refer to Supporting Information Section S1 (Table S1.3) for details of the pretreatment. The composition and yield of the producer gas were not reported in ref 279; however, the data can be found in an earlier publication.[280]

Rice Straw: No publications were found for O_2-blown rice straw gasification in a fluidized bed reactor. Bhattacharya et al.[281] performed a theoretical exergy analysis of hydrogen production from rice straw based on oxygen-blown gasification. The ideal simulation conditions for hydrogen production with oxygen concentration of 95% and an equivalence ratio (air-to-fuel) of 0.25 yielded ~108 g of hydrogen produced per kg of dry ash-free rice straw and a cold gas efficiency of ~70%.

Lee[282] studied the gasification of rice straw in a fluidized bed reactor with steam or stream-O_2 mixtures as gasifying agent. The effect of the oxygen concentration on the gas composition is displayed in Table 21 at a reaction temperature of 800 °C and steam to biomass ratio of ~0.5. As the amount of oxygen increases, the concentration of hydrogen in the producer gas decreased while the amounts of CO and CH_4 increased. When steam alone was used as gasifying agent, the H_2/CO ratio of the producer gas was ~2.8, dropping to 1.9 when 3 vol % O_2 was added and 1.4 when 5 vol % O_2 was added to the steam. The gas yields were not reported.

Yu et al.[283] used an entrained flow lab-scale reactor to study the effect of oxygen enriched air (21−60 vol % O_2, equivalence ratio 0.15−0.35) on the composition of the producer gas over the temperature range of 800−1200 °C. The main findings were that using oxygen enriched air increased the yield of hydrogen, the heating value of the producer gas, and the H_2/CO ratio while reducing the tar concentration. The maximum H_2/CO ratio (1.0) was achieved when an oxygen concentration of 50% was used. The resulting lower heating value (LHV) of the producer gas was ~8.5 MJ/Nm^3 and the gas yield was ~0.88 Nm^3/kg. Although a H_2/CO ratio of 1.0 is too low for gasoline to diesel production, it is suitable for production of alcohols via FT synthesis.

Rice Husks/Hulls: Su et al.[284] used a fluidized bed reactor to study the effect of oxygen on the steam gasification of risk husks. The influence of feedstock, steam to biomass ratio (S/B), equivalence ratio (ER), temperature, bed material, and secondary oxygen supply on the gas yield and composition were also examined. The main findings were that feedstocks with greater C and H contents generate producer gas with higher concentrations of H_2 and CO and less tar. The H_2 yield increased with increasing temperature, reaching a maximum with an ER of 0.27 and S/B of 0.6. Limestone and dolomite bed materials improved tar cracking and increased the H_2 yield compared to olivine bed material but resulted in higher ash content due to attrition of bed material and carryover from the bed. Adding secondary oxygen into the freeboard significantly improved the gas quality and reduced tar concentrations. The results are summarized in Table 22.

The results in Table 22 show that all the feedstocks generate a producer gas with similar composition, with H_2 concentrations of 22.5−30.8 vol % and CO concentrations of 31.7−35.5 vol %. Note that rice husks producer gas has values at the low end of the range.[284] Although the H_2/CO ratios are <1.0 and therefore not suitable for FT synthesis of gasoline to diesel, the concentrations of CO are relatively high compared to steam gasification in the absence of oxygen (typically 15−20 vol %). Therefore, by using the WGS reaction, a gas suitable for FT synthesis can be produced. Reforming methane and tar

Table 21. Oxygen Effect on the Gasification of Rice Straw at 800 °C with a Steam to Biomass Ratio of ~0.5[a]

O_2 (vol %)		0	3	5	7	10	20	30
gas composition (vol %)	H_2	57.5	49.0	41.5	29.6	22.3	21.3	20.9
	CO	20.3	26.1	30.0	38.0	41.1	37.6	31.7
	CO_2	14.0	14.3	20.8	20.6	24.5	29.6	38.4
	CH_4	4.3	7.6	6.5	9.1	8.7	8.4	6.3
	C_{2+}	4.0	3.0	3.2	2.7	3.4	3.1	2.7

[a] Reprinted from ref 282. Copyright 2001 American Chemical Society.

Table 22. Experimental Results from Oxygen-Steam Gasification of Various Biomass Feedstocks (ER = 0.29, S/B = 0.5)[a]

	temperature (°C)		producer gas composition (vol %)					tar
feedstock	Tb	Tf	H_2	CO	CO_2	CH_4	C_2H_m	(g/m^3)
sawdust A	848	673	24.1	33.7	29.8	5.8	2.2	8.0
sawdust B	861	691	25.7	35.1	26.9	5.6	2.1	7.2
straw	821	664	23.1	32.4	31.7	6.0	2.3	12.4
corncob	856	658	24.6	33.6	29.6	5.6	1.9	10.5
rice husk A	816	627	22.5	31.7	32.7	6.3	2.5	13.5
rice husk B	839	669	23.7	32.9	30.7	5.9	2.3	8.4
wood pellets A	874	654	28.3	33.1	27.1	4.9	1.8	6.9
wood pellets B	861	647	27.7	34.1	26.3	5.5	1.9	7.5
straw pellets	831	631	25.6	32.7	29.5	5.8	2.1	8.7
RDF A	907	702	30.8	35.5	23.7	4.4	1.5	5.9
RDF B	891	694	29.7	34.8	25.2	4.5	1.6	6.2

[a] Reprinted from *Journal of Fuel Chemistry and Technology* Vol. 40, (3), Su, D.; Liu, H.; Zhou, Z.; Yin, X.; Wu, C., Biomass gasification with oxygen and steam in a fluidized bed gasifier. p 309, Copyright 2012, with permission from Elsevier (ref 284). The composition of the feedstocks can be found in the "fuel properties" section in Supporting Information Section S1, Table S1.7. Tb, bed temperature; Tf, freeboard temperature.

Table 23. Composition of Fuel Gas as a Function of the Oxygen Content in the Gasification Medium[a]

	combustible gas composition (vol %)					
gasification agent	CO_2	CO	CH_4	H_2	O_2	N_2
steam-air	10.57	20.52	1.35	25.21	0.16	42.19
steam-air +5 vol % O_2	11.97	21.42	1.49	26.01	0.27	38.84
steam-air +10 vol % O_2	13.72	21.95	1.53	27.09	0.18	35.93
steam-air +20 vol % O_2	15.74	23.71	1.65	29.73	0.28	28.89
steam-air +30 vol % O_2	17.82	24.88	1.81	32.10	0.20	23.19
steam-air +50 vol % O_2	18.31	28.79	2.21	37.05	0.49	13.15

[a] Reprinted by permission from SC BIBLIOTECA CHIMIE SA, *Revista de Chimie*, Aspects regarding the use of sorghum by gasification, *62* (1), 116–117, Vladan, S. I., Isopencu, G., Jinescu, C., Mares, A. M., 2011 (ref 287).

could also improve the H_2 and CO availability and H_2/CO ratio. The gas yields, necessary in estimating fuel potential, were not reported however.

Liu and Jin[285] simulated rice husk and wood sawdust gasification in a fluidized bed reactor. With the aim of determining optimized reaction conditions that could reduce problems related to excessive tar production in biomass gasification plants recently constructed in China. The use of oxygen enriched air was compared with pure oxygen in combination with steam. They proposed and simulated a two-stage gasification process where the first stage operated at a low temperature (600–700 °C) and a pressure of 0.3–0.4 MPa using oxygen at a purity of 90% (ER = 0.25). The producer gas was then further reacted with oxygen enriched air in the cyclone at a temperature of 1200–1300 °C, which completely destroys tars and melts the ash to produce a relatively clean gas. The gas was then passed through a steam reformer (S/B 0.1–0.2) and the hydrogen-rich reformate was directed to a catalytic hydrocarbon synthesis reactor to produce a methane enriched gas.

Gas yields were calculated from the gas volume predicted at exit of the first stage (before steam injection). Wood sawdust yielded a maximum of 1.83 m^3/kg using 90% oxygen purity, ER = 0.23. The heating value of the gas was 11.5 MJ/m^3.[285] For rice husks under the same conditions, the gas yield was 1.40 m^3/kg with a heating value of 11.52 MJ/kg. The gas compositions predicted by the simulation were not reported.

Eucalyptus: No papers were identified for gasification of eucalyptus in an oxygen-blown fluidized bed at atmospheric pressure. A related study reported the production of liquid fuels (gasoline to diesel) from eucalyptus (the species was not stated). A fixed bed downdraft gasifier with oxygen enriched air was used, followed by FT synthesis of liquid fuels from the producer gas.[286] The addition of CO_2 to the O_2-enriched air improved the producer gas yield by *X*% (relative) and increased the CO concentration. When the gasification medium had a volumetric composition of 19.1% N_2, 63.4% O_2, and 17.5% CO_2, carbon conversion was ~90%, with a producer gas composition (vol %) of 27.9% H_2, 40.4% CO, 21.2% CO_2, 4.0% CH_4, and 5.5% N_2. The water–gas-shift reaction, desulfurization, and CO_2 removal was used to condition the producer gas so that it was suitable for FT synthesis.

FT synthesis was performed at 4 MPa, at 290–320 °C using a Ru/Mn/Al_2O_3 catalyst.[286] Conversion of CO and H_2 was ~74% and 84% respectively, producing a liquid fuel that contained ~81% hydrocarbons with a chain length (carbon number) of five or greater. The space time yield of >C5 hydrocarbons was ~1.8 kg/(kg-cat h).

Sorghum: One publication related to the oxygen-blown gasification of sorghum DDG using a fluidized bed reactor was found.[278] However, the study was focused on developing a mathematical model of fluid dynamics, heat transfer, and reaction kinetics when using mixtures of oxygen and steam as gasifying medium. That work was briefly discussed in the steam gasification section above.

Vladan et al.[287] gasified sorghum pellets in a pilot-scale (25 kg/h) updraft fixed bed reactor using steam plus oxygen enriched air at 950 °C. The type of sorghum (fiber, grain, or sweet) used in the experiments was not stated. The composition of the producer gas as a function of oxygen addition is listed in Table 23. Although the focus of the

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publication was on the generation of a fuel gas for combustion, the gas composition appears to be suitable for FT synthesis of liquid fuels when O_2 is added to the gasification medium. The gas yields were not reported.

Energycane, *Sesbania*, and Glyricidia (Gliricidia): No papers were identified.

Oxygen Blown, Directly Heated, High-Pressure, Fluidized Bed Gasification: Sugar cane Bagasse: Walter et al.[288] made a theoretical study of the production of second generation biofuels and electricity from Brazilian bagasse via a gasification-FT pathway. It was assumed that gasification-FT or hydrolysis was integrated with a conventional distillery for ethanol production based on fermentation of sugarcane juice. The gasification-FT route was determined to be slightly more energy efficient than the hydrolysis route as well as offering opportunities for product diversification.[288]

Petersen et al.[289] reported a theoretical study (energy efficiency, pinch point analysis, and life cycle analysis) comparing gasification-FT with two biological pathways (separate vs simultaneous hydrolysis and fermentation) for producing liquid fuels (gasoline and diesel via FT and ethanol via fermentation) from South African sugarcane bagasse. The gasification process was assumed to be oxygen and steam blown operating at ~800 °C; however, no mention is made of the pressure or reactor type (fluidized bed, updraft, etc.).[289] The gasification-FT process was determined to have a higher energy efficiency (52−56%) and lower environmental impacts relative to the fermentation pathway (~40−44% efficiency). The energy efficiency of the FT process is in reasonable agreement with the literature (four sources were cited) ranging from 40 to 53%. The energy efficiency of the hydrolysis and fermentation pathways (including four literature sources) range from 40 to 50%.

In a separate study, Petersen et al.[290] conducted a TEA of methanol production via gasification-FT for South African sugarcane bagasse and trash (straw). The assessment was based on integration with an average sized sugar mill (300 wet ton/h sugarcane). Comparisons were made for allothermal vs autothermal gasification, steam vs oxygen blown, as well as high pressure vs atmospheric pressure. The analysis suggested that steam blown atmospheric gasification was more efficient for methanol production and had the lowest costs. Nonetheless, they concluded that the process was not financially viable for private investors.

No relevant publications were identified for the other feedstocks under these reaction conditions.

Oxygen Blown, Directly Heated, High-Pressure, Downdraft Gasification: Sugarcane Bagasse: Leibbrandt et al.[291] used a thermodynamic equilibrium model to predict the composition of producer gas from oxygen blown downdraft gasification under different operating conditions. The effects of temperature, pressure, moisture content, steam to biomass ratio, and equivalence ratio were examined. The feedstocks were bagasse (based on South Africa bagasse) and a pyrolysis slurry from bagasse (note: it is unclear how a slurry could be fed into a downdraft gasifier, the feeding system is not described in the publication). The system boundaries were studied to examine their effect on energy efficiency and producer gas composition. An account was also provided of the trade-offs between operating at conditions which yield the greatest energy efficiency against those that generate producer gas with the H_2/CO ratio of 2 required for FT synthesis of liquid fuels.[291]

No relevant publications were identified for the other feedstocks under these reaction conditions.

Oxygen Blown, Directly Heated, Atmospheric Pressure, Updraft Gasification: Sugarcane Bagasse: De Filippis et al.[292] performed bench scale experimental studies on Cuban sugarcane bagasse using a two-stage oxygen and steam blow, atmospheric pressure gasifier operating at ~800 °C. The reactor used an updraft configuration with a fixed bed second stage packed with either a nickel based catalyst or alumina (noncatalytic). Results are reported for the producer gas composition and yield as well as char and tar yields. Thermodynamic predictions were also used to assess the energy efficiency of the process.[292] **Glyricidia (Gliricidia):** Fernando & Narayana[293] modeled the fluid dynamics for an updraft gasifier and compared it's performance against experimental results obtain using gliricidia as feedstock. A lab-scale air blown updraft gasifier was used for the tests. The maximum yields of CO and H2 were ~0.23 and ~0.08 Nm3/kg dry gliricidia, respectively. No relevant publications were identified for the other feedstocks under these reaction conditions.

3.2.2. Fast Pyrolysis.

Pyrolysis is a highly versatile process that can be optimized for the production of char, liquids (oils/tars), or gases depending on the feedstock, reactor configuration, and reaction conditions.[294−297] In some regards, pyrolysis is a mature technology. However, the more advanced processes, such as fast-pyrolysis and catalytic fast-pyrolysis, for producing liquid fuels from biomass feedstocks are still under development and are yet to be proven at commercial scale.[250,262,297] A useful review on historical developments of pyrolysis reactors has been reported.[298] A number of companies are now offering "off the-shelf" fast-pyrolysis units at scales up to 400 Mg/day dry input (~80 MW_{th}).[262,299] However, due to a lack of operational commercial facilities and the proprietary nature of cost and efficiency data, limited information is available.

Biomass pyrolysis oil, here after referred to as "bio-oil", has the potential to be upgraded by hydrotreatment or other catalytic processes to produce alternative transportation fuels (gasoline, diesel, and jet-fuel). However, these methods have yet to be demonstrated at commercial scale or proven to be financially viable.[250,262,297] For example, one of the leading fast pyrolysis companies (KiOR) went bankrupt in late 2014 soon after they attempted to commercialize a catalytic process to produce liquid fuels from biomass fast-pyrolysis oil. It is not clear however whether the bankruptcy was directly related to the costs involved with commercializing their catalytic fast pyrolysis process or due to other reasons.

Bio-oil is a complex mixture of oxygenated hydrocarbons and contains a significant amount of water. This is in contrast to coal or petroleum derived pyrolysis oils which contain practically no oxygen or water. The amount of water in a typical bio-oil is 20−30 wt % when the starting biomass has a moisture content of ~7 wt % (the value often used for biomass fast-pyrolysis in industrial processes). A dry biomass starting material can reduce the water in the bio-oil to 5−15 wt % (pyrolysis water). It is important to note that water cannot be removed easily from bio-oils without significant energy losses. Evaporation of water is *not* possible as this causes the bio-oil to degrade.[7,297]

Bio-oil is a brown liquid with approximately the same ratio of carbon, hydrogen, oxygen, and nitrogen as the parent biomass. A maximum of ~70 wt % of the starting dry biomass is converted to bio-oil.[296,297,300] The bio-oil contains a maximum of ∼65% of the energy in the "as-received" parent biomass based on $LHV_{a.r}$ and feedstock and bio-oil moisture contents of 7% and 22%, respectively. When based on the HHV of dry biomass, a maximum value closer to 75% is obtained.

Bio-oils have a lower heating value of 10−17 MJ/kg ($LHV_{a.r}$, M.C. 15−30 wt %), which is less than oxygenated fuels such as ethanol ($LHV_{a.r}$ ∼ 27 MJ/kg, M.C. < 0.1 wt %) and much less than petroleum fuels ($LHV_{a.r}$ 40−50 MJ/kg, M.C. < 0.1 wt %).[301] The maximum yield of bio-oil is approximately 550−625 L/Mg of biomass assuming a mass conversion of 65−75% from the dry biomass feedstock and a bio-oil density of 1.2 kg/L.[301] Further information on mass and energy balance and costs are provided later in this section.

The char from fast-pyrolysis is a black-brown, dry, brittle solid which contains very little water, <5 wt %.[297] It can be a valuable source of carbon (∼15 wt % of starting dry biomass) and energy (∼20−25% of the energy in the starting biomass, $LHV_{a.r}$). The char is typically combusted to provide the heat to drive the pyrolysis reactor. The char can be recovered and exported, but a replacement fuel would be required to sustain the pyrolysis reactions.[7,296,297]

A gas coproduct with similar composition as producer gas from gasification (mainly CH_4, CO, CO_2, and H_2) is generated during biomass pyrolysis and is usually combusted to provide heat to the pyrolyzer or other local heat requirements. The fuel-gas typically accounts for <15 wt % of the dry-feed and contains <10% of the feedstock energy ($LHV_{a.r}$ basis).[7,296,297]

Due to bio-oil's lower energy density and higher oxygen content compared to petroleum derived fuels (Table 24), upgrading is required before it can be used as a replacement for transportation fuels. Bio-oil can be used as feedstock for gasification-Fischer−Tropsch processes to produce biofuels (H_2, methane-SNG, gasoline, diesel, and jet-fuel) and chemicals; however, only limited test results have been reported.[7,296,297] The technical aspects of upgrading bio-oil to liquid fuels is discussed in Supporting Information Section S3, and costs are summarized in section 3.2.2.2.

Table 24. Properties of Wood Derived Bio-Oil, Petroleum Derived Heavy Fuel Oil and No. 2 Diesel[a]

property	bio-oil	heavy fuel oil	no. 2 diesel fuel
moisture content, % wt	15−30	0.1	n/a
pH	2.5	n/a	n/a
specific gravity, kg/L	1.20	0.94	0.85
elemental composition, wt %			
C	54−58	85	86
H	5.5−7.0	11.0	11.1
O	35−40	1.0	0
N	0−0.2	0.3	1
ash, wt %	0−0.2	0.1	n/a
HHV_{dry}, MJ/kg	16−23[b]	40	45
viscosity (at 50 °C), cP	40−100	180	<2.4
solids, wt %.	0.2−1.0	1.0	n/a
distillation residue, wt %	up to 50	1	n/a

[a] Reprinted with permission from Somrang, Y. Effect of Operating Conditions on Product Distributions and Bio-oil Ageing in Biomass Pyrolysis. Ph.D. thesis, Imperial College, London, UK., 2011 (ref 294). Copyright 2011 Imperial College. Reprinted from *Energy Convers. Manage.* Vol. 50 (12), Balat, M.; Balat, M.; Kirtay, E.; Balat, H. Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. pp 3147−3157. Copyright 2009, with permission from Elsevier (ref 296). n/a, not applicable. [b] For bio-oil on an as-received basis, the $HHV_{a.r}$ is ∼11−19 MJ/kg, i.e., with 15−30 wt % M.C.

The final product distribution from fast pyrolysis and the composition of the products are highly dependent on the biomass, reactor type, reactor geometry, and operating conditions such as temperature, vapor residence time at elevated temperature, and pressure.[295,302] The bio-oil vapors and aerosols are separated from char and ash using traditional cyclone filters followed by quenching (cooling/condensing) and electrostatic precipitators (ESP) or fiber filters.[7,297,299] In practice the bio-oil is rarely recovered completely free of ash and char.

3.2.2.1. Fast Pyrolysis Reactors—Mass and Energy Balances. Only transport and circulating fluidized-bed pyrolysis reactors have been commercialized for the production of food flavorings from biomass.[296,297] As commercial-scale pyrolysis reactors for bio-oil production for energy/fuel uses are currently emerging, the selection of the most appropriate reactor type(s) is not yet apparent. Two types of pyrolysis reactor that are potentially suitable for commercial bio-oil production have been operated/tested at demonstration scales of ∼10−200 Mg/day dry biomass input (2−40 MW_{th}): (i) fluidized-bed and (ii) rotating cone.[296,297] These two reactor types have been described in detail elsewhere.[262,297] A brief technical description of these reactors is provided in the Supporting Information, Section S3.

Mass and Energy Balance for Bubbling Fluidized Bed (BFB) Reactors: Although this type of reactor is the most widely studied for bio-oil production, limited peer-reviewed information is available regarding mass and energy balances for large units. A thorough account of the information available as of mid-2012 has been reported;[262] the main findings are summarized below.

Based on the available information from various technology providers and researchers,[7,296,297] bubbling fluidized-beds typically produce a maximum bio-oil yield of 60−70 wt % from woody biomass on a dry-feed basis, accounting for about 70% of the feedstock energy content (basis not reported). The char accounts for about 10−15 wt % but contains about 25% of the energy in the starting biomass (basis not reported). The fuel-gas yield is between 15 and 20 wt % and contains about 5−10% of the energy in the starting biomass (basis not reported).[7,296,297] The net thermal efficiency (fuel-basis) is typically reported to be 60−70% (basis not reported).[7,296,297] No reports for the net or gross thermal efficiency on a "process-basis" were identified.

Due to the lack of information, it is not possible to present a meaningful energy balance that would distinguish this reactor type from alternative designs. Therefore, the generic Eff_{N-FB} of 65% (net-fuel basis, see Supporting Information Section S4 for definitions) can be assumed as a reasonable upper estimate for BFB processes (based on $LHV_{a.r}$ and M.C. of starting biomass 6−10 wt %). When based on HHV_{dry}, the Eff_{N-FB} is approximately 75%.

Summary of General Circulating Fluidized Bed (CFB) TEA Studies: A number of detailed techno-economic, design cases and life cycle assessments for biomass fast-pyrolysis using a circulating fluidized-bed reactor and hydro-processing to upgrade the bio-oil have been published.[303−306] Techno-economic information has also been reported from a European Union[307] funded project in 2000 where two types of fast-pyrolysis reactors were compared at a scale of 200−250 kg/h dry wood input (5−6 Mg/day).[305] The rotating cone reactor (included as one of the reactor types and operated by Biomass Technology Group[308]) is still operational and is discussed in the following subsection.

A thorough report was published in 2009 detailing a plant design for 2 000 Mg/day (dry, poplar woodchips input) for fast-pyrolysis followed by hydrotreating and hydrocracking processes to produce "drop-in" gasoline and diesel.[304] Detailed heat and material balances as well as equipment cost estimates were reported. That study was followed by a life cycle assessment in 2011[306] for the same process. The findings from these studies that are related to costs are summarized in section 3.2.2.2.

It is worth noting that these two independent studies (supported by EU[305] and U.S.[304,306] funds) decided upon the same processes for converting biomass into transportation fuels, and this approach has attracted the most attention in the published literature, i.e., using a CFB followed by hydrotreatment.[303−306,309] Some recent studies are those published by Michigan Technical University and UOP LCC in 2011 and Energia Institute (IMDEA), Spain, in 2012. The former is a life cycle assessment (LCA) of electricity generation from fast-pyrolysis bio-oil,[303] and the latter is an LCA of transportation fuels from biomass pyrolysis.[309]

Mass and Energy Balance for CFB Reactors: A detailed breakdown of the mass and energy balances for UOP's CFB reactors are provided in Supporting Information Section S3. In summary, the balances are in general accordance with the above-mentioned literature on circulating fluidized-bed technologies. From the information available, it is not possible to make a meaningful distinction between the mass and energy balances of BFB and CFB designs. Table 25 summarizes the approximate (generic) heating values ($LHV_{a.r}$ and HHV_{dry}) of harvested biomass (M.C. 50−60 wt %), pelletized biomass, and the products from fast-pyrolysis along with typical mass and energy balances. It should be noted that changes in the biomass feedstock or reaction conditions results in a pyrolysis oil (bio-oil) with different properties.

Table 25. Approximate Heating Values and Mass and Energy Balances for Biomass and Fast Pyrolysis Products[a]

		heating value		balances	
properties	moisture content	$LHV_{a.r}$	HHV_{dry}	mass[b]	energy[c]
units	wt %	MJ/kg	MJ/kg	%	%
fresh biomass	50−60	6−9	15−20	100	100
fast-pyrolysis oil (bio-oil)	15−30	10−17	16−23	65−75	60−75
fast-pyrolysis char	1−5	∼32	∼33	10−20	15−25
fast-pyrolysis gas (fuel-gas)	0	5−14	6−15	10−25	5−15

[a] Using data from refs 7, 296, 297, 300, 310, and 311. [b] On a dry basis. [c] Energy balance, i.e., energy in the product divided by that in the starting material, without accounting for the energy required for processing, on HHV_{dry} basis.

Mass and Energy Balance for Rotating Cone Pyrolyzers: Mass and energy balances have been reported for a typical rotating cone pyrolysis unit (25 $MW_{th(input)}$, ∼150 Mg/day dry biomass input, LHV_{dry} 14.7 MJ/kg).[310] Maximum bio-oil yields are 60−70 wt % of the dry-feed, fuel-gas ∼20 wt %, and char ∼10 wt %. The energy contents of the bio-oil, char, and fuel-gas are approximately 66%, 26%, and 8% of the $LHV_{a.r}$ of the biomass feedstock, respectively. The moisture content of the biomass feedstock was 27 wt % and the bio-oil moisture content was 22 wt %. All char is consumed to provide heat to the pyrolyzer.[310]

The $Eff_{N\text{-}FB}$ is stated to be 66% and the $Eff_{G\text{-}PB}$ as 64% when utility energy is accounted for, based on $LHV_{a.r}$ and moisture contents as above.[310] As bio-oil is the only product and the entire thermal requirements for the plant come from the char and fuel-gas, the gross and net efficiencies on a fuel-basis are equal, as are the net and gross efficiencies on a process-basis. The 2% difference between "fuel-basis" and "process-basis" efficiency are due to electricity requirements,[310] and definitions of these terms are provided in Supporting Information Section S4.

Summary of Fast-Pyrolysis Reactors: The mass and energy balances presented above for fast-pyrolysis reactors are the best estimates based on the available information at the time of writing. It became apparent that definitive values or conclusions are hard to obtain. Due to the complex nature of the pyrolysis process and its versatility, any of the reactor types summarized above could be operated with slightly different conditions or feedstock to produce significantly different mass and energy balances. Care needs to be taken when comparing efficiencies from one process to another to ensure a common basis.

In general, the efficiency of fast-pyrolysis is within the range of 60−70% when based on $LHV_{a.r}$[7] and 70−80% when based on HHV_{dry}. Table 26 provides a breakdown of these efficiencies in terms of net, gross, and fuel- and process-based values. The net efficiency is approximately 5% lower than the gross to account for additional energy that could be recovered from the char and/or fuel-gas in a fully integrated commercial-scale facility. The net efficiencies relate to a process where the bio-oil is the only exportable product and contains 15−25 wt % of water. Elsewhere, net process-based efficiencies of 70−90% have been reported for generic fast-pyrolysis systems[312] and references therein or even 95%.[313] However, these values are unlikely to be achieved at commercial-scale facilities.

Table 26. Approximate Efficiencies for Bio-Oil Production from a Generic Fast-Pyrolysis Reactor[a]

basis		symbol	$LHV_{a.r}$[b]	HHV_{dry}
fuel	net	$Eff_{N\text{-}FB}$	65	75
	gross	$Eff_{G\text{-}FB}$	70	80
process	net	$Eff_{N\text{-}PB}$	60	70
	gross	$Eff_{G\text{-}PB}$	65	75

[a] All values have a deviation of ±10% absolute. [b] Where the M.C. of starting biomass is 6−10 wt % and the bio-oil M.C. is 15−25 wt %.

The main challenge to improving the efficiency and cost of bio-oil production is controlling the chemistry of the pyrolysis process via the use of catalysts and reaction conditions inside the reactor. Fundamental work is still required to better understand and control biomass fast-pyrolysis processes.[7,297,314] Likewise, fundamental information regarding the molecular properties of bio-oil needs to be improved so that more efficient pyrolysis and upgrading processes can be designed.[7,314]

Most of the current research is conducted on the pyrolysis reactor design, although this only accounts for about 10−15%

of the capital cost of the entire plant.[7] More emphasis should be placed on understanding the fundamentals of pyrolysis chemistry and reducing pretreatment, recovery, stabilization, and upgrading costs.

3.2.2.2. Economic Evaluation of Fast-Pyrolysis. In this section, cost data for producing bio-oil is discussed. This is followed by cost estimates for upgrading bio-oil to a "drop-in" replacement for transportation fuels.

Cost Estimates for Producing Bio-Oil: Cost data for pyrolysis modules varies significantly between literature sources and depends on the reactor type. An estimate of the lowest and highest cost ranges has been published for a normalized 25 $MW_{th(input)}$ (~350 Mg/d input of biomass with 50% M.C., $LHV_{a.r}$ 6.2 MJ/kg) pyrolysis unit, which includes feedstock preparation, dryer, hammer mill, rotating cone pyrolysis reactor, gas cleaning, and bio-oil recovery.[310] The capital investment costs were between \$5.6 and 14.4 million. Production costs, excluding the cost of feedstock, were given as \$94–188/Mg of bio-oil (Table 28), which is equivalent to \$7.5–15/GJ (published 2008).[310]

A summary of the techno-economic study from Uslu et al.[310] is reproduced in Tables 27 and 28 for fast-pyrolysis for bio-oil production and for conventional biomass pelletization as methods to increase the density of biomass feedstocks. In this economic evaluation, a scale of 40 $MW_{th(input)}$ (560 Mg/day input of biomass) at 50% M.C., and a $LHV_{a.r}$ 6.2 MJ/kg was used to normalize the data for the two processes shown in Table 27 to a common basis for analysis and comparison. In the accompanying sensitivity analysis, it was noted that the economies of scale have considerable influence on production costs. For pyrolysis processes, capacities greater than 25 $MW_{th(input)}$ (~350 Mg/day input of biomass with 50% M.C., $LHV_{a.r}$ 6.2 MJ/kg) do not benefit greatly from economies of scales (although costs do continue to decrease).[310]

Table 27. Technical Comparison of Pyrolysis and Pelletization Processes[a]

		pyrolysis	pelletization
feedstock	unit	clean wood waste	green wood chips
moisture content (M.C.)	wt %	-	57
LHV (as-received)	MJ/kg	6.2	6.2
product type		bio-oil	pellets
product M.C. (average)	wt %	20–30 (~22)	7–10
product $LHV_{a.r}$ (dry)	MJ/kg	17	15.8 (17.7)
bulk mass density	kg/m^3	1200	500–650
bulk energy density	GJ/m^3	20–30	7.8–10.5
thermal efficiency[b]	$LHV_{a.r}$	66%	92.2%
net efficiency[c]	$LHV_{a.r}$	64%[d]	84%[e]

[a] Reprinted from *Energy*, Vol. 33, Uslu, A.; Faaij, A. P. C.; Bergman, P. C. A., Pre-treatment technologies, and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation. pp 1206–1223, Copyright 2008, with permission from Elsevier (ref 310). [b] Net fuel-based efficiency indicates the efficiency where utility use is not included (energy of product/energy of feedstock), i.e., as defined in Supporting Information Section S4. [c] Net process-based efficiency includes primary (utility) energy used to produce power necessary for components in the plant, i.e., as defined in Supporting Information Section S4. [d] Pyrolysis electricity consumption is accepted as 0.015 MW_e/MW_{th}; electricity is assumed to be generated with 40% efficiency. [e] The utility fuel consumption is assumed as 11.3 MW_{th} and electric consumption as 1.84 MW_e for 170 000 Mg/year input. Using sawdust yields a net efficiency of ~88%.

Table 28. Economic Comparison of Pyrolysis and Pelletization Processes ([a])

	unit	pyrolysis	pelletization
normalized capacity	$MW_{th(input)}$	40	40
capital investment	M\$	7.8–19.9	7.8
specific investment	M\$/$MW_{th(input)}$	0.20–0.50	0.19
O&M[c]	%	4	5
energy consumption	kWh/$Mg_{(input)}$	75	129
production cost[b]	\$/Mg	94–188	67.5
production cost[b]	\$/GJ	7.5–15.0	4.3

[a] Feedstock cost is not included, converted from € to \$. Reprinted from *Energy*, Vol. 33, Uslu, A.; Faaij, A. P. C.; Bergman, P. C. A., Pre-treatment technologies, and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation. pp 1206–1223, Copyright 2008, with permission from Elsevier (ref 310). [b] Assumptions for pyrolysis 7 500 h load factor, 15-year depreciation; and for pelletization 7 884 h/year load factor. Feedstock cost is excluded. [c] O&M, operation and maintenance.

The data presented in Tables 27 and 28 assume a facility with 40 MW_{th} input. This corresponds to 560 Mg/day of freshly harvested biomass (50% moisture content and $LHV_{a.r}$ of 6.2 MJ/kg) or ~200 000 Mg/year.

A study published in 2011 estimated the cost of production of bio-oil by fast-pyrolysis.[297] The assessment includes the complete installation costs, from dry-feed preparation through product bio-oil storage (ready for transport). Figure 22 shows the estimated cost (\$/Mg) for bio-oil production at different throughput, starting at 1 000 Mg/year biomass dry-feed and considering four different biomass feed costs (0, 40, 60, and 100 \$/Mg). Assumptions used in the calculation are that 75% of dry wood (by weight) is converted to bio-oil, and capital costs are based on 2011 prices.[297] Note that the type of pyrolysis unit was not identified.

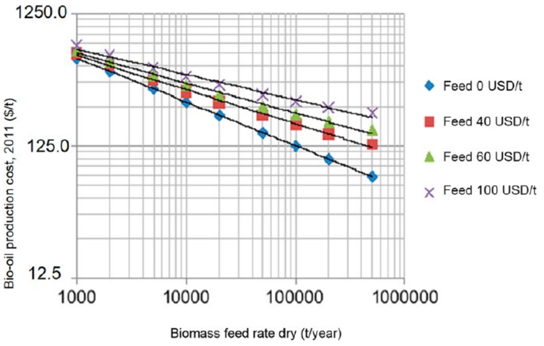

Figure 22. Bio-oil production costs (units in metric tonnes). Reprinted from *Biomass Bioenergy* Vol. 38, Bridgwater, A. V. Review of fast pyrolysis of biomass and product upgrading. pp 68–94, Copyright 2011, with permission from Elsevier (ref 297).

Based on the economic assessment presented in Figure 22 it can be estimated that the cost of bio-oil production is roughly \$750/Mg in the worst case (biomass feed rate 1 000 Mg/year at \$100/Mg). Bio-oil would have to be produced from a dry-biomass feed rate of approximately 10 000 Mg/year (27 Mg/day) to realize production costs of ~\$250 to \$380/Mg, depending on feedstock cost. This scale of production is feasible with current technology. State-of-the-art, commercially available (or near commercial availability), fast-pyrolysis units on a dry-feed basis are

Circulating FB = 400 Mg/day (140 000 Mg/year or 116 000 Mg/year$_{80\%}$)
Envergent

Bubbling FB = 200 Mg/day (70 000 Mg/year or 58 000 Mg/year$_{80\%}$)
RTI/Dynamotive

Rotating Cone = 120 Mg/day (44 000 Mg/year or 35 000 Mg/year$_{80\%}$)
BTG

Mg/y$_{80\%}$ refers to an operating availability of 80% of the year, 292 days per year; Mg/y is 365 days.

From the data reproduced in Table 28, the estimated cost of bio-oil production is \$94 to 188/Mg at a scale of 40 MW$_{th}$ (560 Mg/day biomass input with 50% moisture and LHV$_{a.r}$ of 6.2 MJ/kg).[310]

A comprehensive review article from 2006 estimated the minimum selling price for fast-pyrolysis bio-oil as \$145/Mg and with continued R&D it could potentially reach \$110/Mg.[7] The minimum selling price accounts for capital costs, fixed and variable operating costs, and a feedstock cost of \$60/Mg$_{(dry)}$. At a scale of 1 000 Mg/day dry biomass input, the capital investment was reported to be \$50 million, with the potential of being reduced to \$26 million with continued R&D.

Cost Estimates for Upgrading Bio-Oil to Transportation Fuel: The majority of the available information on upgrading bio-oil to produce transportation fuels is based on a circulating fluidized-bed fast-pyrolysis reactor with upgrading via hydrotreatment.[7,304,305,309] A thorough report of a design case for this process was published in 2009 by Pacific Northwest National Laboratory.[304] It was concluded that the capital cost for a standalone plant (biomass to finished fuel) with a capacity of 2 000 Mg/day dry biomass input, producing 76 million gallons of gasoline and diesel, would be \$303 million (2007 basis). The minimum fuel selling price was \$2.04/gal to achieve a 10% return on investment. Colocating the plant with an existing refinery could reduce the capital investment to \$188 million and the minimum fuel selling price to \$1.74/gallon. It should be noted that the scale considered in the design case[304] is 2 000 Mg/day input dry biomass. At a smaller scale (500 Mg/day input dry biomass), the minimum fuel selling price increases to \$2.68/gallon. Capital cost for the 500 Mg/day unit was not given.[304]

A scale of 500 Mg/day dry biomass input is large for a single fast-pyrolysis facility in Hawai'i; however, it is within the range that is feasible (cf. ref 262). The cost estimate for gasoline and diesel production at this scale is ~\$3/gallon (2007 price[304]). Still, it should be noted that the cost estimates are based on forward-looking assumptions regarding improvements in technology that could be achieved by 2015 and a plant design at the "*n*th" state of development.[304] Therefore, the cost estimates should only be considered as indicative.

In an earlier review article (2006), the minimum selling price for finished products (gasoline and diesel) from bio-oil upgrading via hydrotreatment was estimated to be \$2.2/gallon with the potential of being reduced to \$1.8/gallon with continued R&D.[7] The minimum selling price accounts for capital as well as fixed and variable operation costs and a feedstock cost of \$60/Mg$_{(dry)}$. The total capital investment (for fast-pyrolysis, crude upgrading, and product finishing) was reported to be \$110 million with the potential of being reduced to \$60 million with continued R&D. This was for a scale of 1 000 Mg/day dry biomass input.

Gasification-FT of Bio-Oil: The cost of producing transportation fuels from bio-oil with upgrading achieved via oxygen blown entrained flow gasification-FT (EFG-FT) synthesis has been evaluated (FT conversion efficiency was assumed to be 71%).[310] The cost was estimated to be \$12.3/GJ$_{HHV}$ when accounting for the entire processing and delivery chain, from feedstock harvest and logistics through to production of transportation fuels.[310] Based on 1 L of diesel containing 38 MJ of energy (HHV), the cost of production is approximately \$1.8/gallon of diesel equivalent fuel. This assessment was published in 2008, and the cost estimate includes shipping the bio-oil from South America to Western Europe (~7 000 miles).[310]

A breakdown of the cost estimates for producing FT-liquids from bio-oil alongside those from biomass pellets and torrefied and pelletized biomass (TOP) is presented in Table 29. The related net process-based efficiencies were also assessed. It was reported that the highest efficiencies are 61% for FT-liquids from TOP. Bio-oil FT-liquids could be produced at 44% efficiency. These values were based on conversion efficiencies (based on LHV$_{a.r}$) for FT-liquids via EFG-FT of 71%.[310]

Table 29. Cost of Chains Delivering FT-Liquids from Different Pretreatment Processes[a]

step in the chain	TOP	pelletization	pyrolysis (rotating cone)
product	FT liquids		
units	\$/GJ$_{HHV}$ liquids (biofuel)		
conversion[b]	3.9	3.6	3.4
storage	0.3	0.3	1.6
ship (7 000 miles)	1.1	1.6	1.4
truck (60 miles)	2.1	2.4	3.6
biomass production	1.9	2.0	2.3
total cost	9.3	9.9	12.3
total cost (\$/gal)[c]	1.3	1.4	1.8

[a](\$/GJHHV liquid fuel delivered). Reprinted from *Energy*, Vol. 33, Uslu, A.; Faaij, A. P. C.; Bergman, P. C. A., Pre-treatment technologies, and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation. pp 1206−1223, Copyright 2008, with permission from Elsevier (ref 310). [b]Conversion includes pretreatment and final conversion. [c]Cost converted from \$/GJ$_{HHV}$ to \$/gallon based on HHV of 44.7 MJ/kg (diesel), volumetric mass of 0.31 gallons per kg, giving 6.9 gallons of diesel per GJ$_{HHV}$.

3.2.2.3. Summary of the Techno-Economic Assessment of Fast Pyrolysis. The cost of producing bio-oil from literature sources ranges from approximately: (i) \$100−150/Mg in 2006 including all costs;[7] (ii) \$100−200/Mg in 2008 excluding capital investment costs and feedstock cost;[310] (iii) \$250−750/Mg in 2011 including capital costs;[297]

When "drop in" transportation fuels are considered as the final product from bio-oil, cost estimates range from (i) ~\$2/gallon in 2008 using EFG-FT (feedstock and capital costs for EFG-FT plant were not accounted for);[310] (ii) ~\$2/gallon in 2006 using hydrotreatment (including all costs);[7] (iii) ~\$3/gallon in 2009 using hydrotreatment (not accounting for capital costs),[304]

A summary of a techno-economic assessment for producing pretreated biomass, i.e., bio-oil, torrefied biomass, torrefied and pelletized biomass, and biomass pellets is presented in Table 30. The main factors influencing production costs were

Table 30. Techno-Economic Comparison of Torrefaction, TOP, Pelletization, and Pyrolysis (Bio-Oil)[a]

	unit	torrefaction	TOP	pyrolysis	pelletization
net efficiency[b]		92%	90–95%	64%	84%
energy content (LHV_{dry})	MJ/kg	20.4	20.4–22.7	17	17.7
mass density	kg/m^3	230	750–850	1200	500–650
energy density	GJ/m^3	4.6	14.9–18.4	20–30	7.8–10.5
specific capital investment	M\$/MW_{th}	0.21	0.24	0.20–0.50	0.19
production cost	\$/Mg	72.5	62.5	94–188	67.5

[a] Reprinted from *Energy*, Vol. 33, Uslu, A.; Faaij, A. P. C.; Bergman, P. C. A., Pre-treatment technologies, and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation. pp 1206–1223, Copyright 2008, with permission from Elsevier (ref 310). [b] Net efficiency, process-based as defined in Supporting Information Section S4.

plantation yield, interest rate (on capital investment), load factor/availability of the conversion facility, and plantation distance from the harbor.[310] The base cases used in the cited study were (i) plantation yield of 22.4 $Mg_{(dry)}$/ha year, (ii) interest rate of 10%, (iii) harvest operation window of 8 months (OW), (iv) distance to harbor of 60 miles.

It was found that increasing the OW to 12 months decreased production costs by up to 25% and increasing the interest rate to 20% increases costs by 33%.[310] Increasing the harvest yield to 150% of the base case decreases cost by up to 11%.[310] Increasing the trucking distance to 120 miles increases costs by up to 20%.[310]

3.2.2.4. Summary and Conclusions for Fast-Pyrolysis. Based on the various technological and economic studies described above it can be seen that the production of bio-oil from biomass fast pyrolysis is technically feasible; however, the upgrading of bio-oil to jet fuel is yet to be demonstrated at a significant scale. It is not straightforward to compare the production costs of bio-oils from different studies as the assumptions and/or bases used are not the same. Moreover, the production costs listed below do not account for capital investment costs and therefore should only be considered as preliminary estimates.

Based on the assessments in refs 7 and 304, transportation fuels produced from bio-oil upgraded by hydrotreatment appears to be competitive against gasoline and diesel prices in Hawai'i (~\$2–3/gallon, 2016). In addition, the cost of transportation fuels produced from oxygen-blown entrained flow gasification followed by FT-synthesis, using bio-oil as feedstock, is approximately \$2/gallon diesel fuel equivalent (Table 29[310]).

If the usable fuel output from a fast-pyrolysis unit is considered in terms of volume, the approximate yield would be 550–600 L (145–160 gallons) of bio-oil per Mg of dry biomass input (assuming mass conversion of 66–72%, density of bio-oil 1.2 kg/L). If the bio-oil is upgraded to "drop-in" replacement transportation fuels, one dry Mg of biomass will produce approximately 340 L (90 gallons, 290 kg), based on current estimates.[299,315] A summary of the yields of bio-oil and transportation fuels that could be produced per kilogram of dry biomass via fast-pyrolysis and hydrotreatment is presented in Table 31 along with their physical properties and costs, based on conservative estimates. The assumptions used to derive the values are provided in the footnote to the table.

Strengths and Weakness of Different Modes of Fast Pyrolysis: Table 32 provides a summary of the strengths and weakness of the various fast pyrolysis reactors that are potentially useful for processing biomass.

3.2.2.5. Fast Pyrolysis of Tropical Biomass Species. Only a limited number of studies have been reported for the fast pyrolysis of tropical biomass species other than rice husks, rice straw, and bagasse. To our knowledge, there are no publications that provide complete mass balances, energy balances, or techno-economic analyses for any tropical biomass feedstocks.

Banagrass: Banagrass is a species of elephant grass (*Pennisetum purpureum Schum*) which is similar to napier grass (*Pennisetum purpureum*). While there are a great number of publications examining the yields and conditions under which these grasses can be grown, there are few reports on their pyrolysis behavior.

A couple of studies were reported by HNEI researchers using a lab-scale bubbling fluidized bed reactor to examine bio-oil yield and composition (in terms of C, H, N, O content) for a number of tropical biomass species including two hardwoods, leucaena and eucalyptus; two grasses, banagrass and energycane (before and after a water leaching pretreatment); and an agricultural residue, sugarcane bagasse.[164,165] All the

Table 31. Mass and Energy Yields and Physical Properties for Bio-Oil and Transportation Fuels Produced per Kilogram of Dry Biomass Input to a Fast-Pyrolysis Reactor, Upgrading via Hydro-Treatment[262]

property	units	bio-oil	transportation fuel
mass	kg	0.70	0.29
moisture	wt %	22.0	0.0
$LHV_{a.r}$	MJ/kg	15.6	42.5
specific density	kg/L	1.2	0.85
volumetric mass	gallon/kg	0.22	0.31
volume	L (dm^3)	0.58	0.34
volume	gallons	0.15	0.09
energy content	MJ	10.9	12.3
energy conversion[a]	%	~65	-
energy density	MJ/gallon	71	137
energy density	GJ/m^3	18.7	36.1
cost	\$/Mg	700	1550
cost	\$/GJ	44.9	36.5
cost	\$/gallon	3.2	5.0

[a] Energy Conversion is for $LHV_{a.r}$ values on a net fuel-basis. Assumptions used: Mass conversions as stated in the table. Specific density from ref 300, $LHV_{a.r}$ derived from HHV_{dry} values of 22 MJ/kg for bio-oil with 6 wt % hydrogen content (which is slightly lower than the value reported in ref 310 of 23.5 MJ/kg HHV_{dry}), and for transportation fuels based on diesel with HHV_{dry} of 44.7 MJ/kg and 11 wt % hydrogen content.[301] Costs were estimated by assuming bio-oil has a production cost of \$700/Mg and transportation fuels \$5.0/gallon. Biomass feedstock assumed to have a HHV_{dry} of 19.5 MJ/kg ($LHV_{a.r}$ 16.8 MJ/kg at a moisture content of 6 wt % and a hydrogen content of 6 wt %). All the other properties were derived using these values.

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Table 32. Summary of the Strengths and Weakness of Different Modes of Fast Pyrolysis

pyrolyzer type	strengths	weaknesses
bubbling fluidized bed	• mature technology • relatively easy to construct and operate • scaling is well understood • produces a relatively stable, single-phase bio-oil • char separation is easier than from circulating FB designs	• At scales >40 MW_{th}, input heat transfer may be an issue. • requires particle size of <3 mm • requires high flow rate of inert gas • requires larger processing equipment than rotating cone design which increases cost and reduces efficiency • limited peer-reviewed information on mass and energy balances for larger reactors
dual fluidized bed	• mature technology • relatively easy to construct and operate • scaling is well understood • potential for greater through-put than BFB • produces a relatively stable, single-phase bio-oil	• requires particle size of 2−6 mm • char separation is more difficult than from BFB • requires high flow rate of inert gas • requires larger processing equipment than rotating cone design which increases cost and reduces efficiency • limited peer-reviewed information on mass and energy balances for larger reactors
rotating cone	• requires less inert gas than FB designs, and unit operations are smaller which reduces costs and increases efficiency • bio-oil recovery is easier than from FB designs	• requires particle size of ~0.2 mm • less mature technology than FB designs • more difficult to integrate with other unit operations in the process which makes construction more complex than FB designs • scaling may be an issue at sizes >25 MW_{th} input

Table 33. Bio-Oil, Char, and Gas Yields (wt % Feedstock; daf, Dry Ash Free) from Lab-Scale Pyrolysis of Eucalyptus, Leucaena, Sugarcane Bagasse, Energycane, Pretreated Energycane (S3), Banagrass, and Pretreated Banagrass (S3) at a Residence Time of 1.5 s[165]

	temperature	dry bio-oil[a]	volatile bio-oil[b]	$char_{org}$[e]	CO, CO_2, CH_4, H_2[d]	undetected[f]
sample	°C	wt %	wt %	wt %	wt %	wt %
eucalyptus	450	48.1	0.1	4.2	6.8	40.8
leucaena	450	40.8	0.3	2.6	6.5	49.9
S-bagasse	450	55.1	<LLQ[c]	2.2	5.6	37.1
E-cane	450	46.8	0.2	3.7	6.3	42.9
E-cane S3	450	55.3	<LLQ[c]	3.5	6.1	35.1
banagrass	450	36.7	0.2	3.0	7.8	52.5
banagrass S3	450	41.3	<LLQ[c]	3.5	7.4	47.8

[a] SD of the "dry bio-oil" yield is < ± 2.0 wt % (absolute). [b] Volatile bio-oil refers to the amount of bio-oil removed from the sample during drying and is determined by analyzing the bio-oil solution by GCMS before drying and again after it is dried. [c] <LLQ, less than the lower limit of quantification, which equates to a yield of less than 2.0 wt % of the "daf" feedstock. [d] Indicative values derived from online gas analysis. [e] The bias in the char yield is estimated to be <±2% (absolute) and SD <±1.5 wt %, see Table 9 for the amount of ash contained within the char. [f] "Undetected" is derived as 100% − (dry bio-oil + volatile bio-oil + char + CO, CO_2, CH_4, and H_2 yields), the undetected material is composed of water and light volatiles lost during drying.

samples were grown in Hawai'i, and details of the pretreatment are provided in Supporting Information Section S1. The product yields from fast pyrolysis are shown in Table 33.

Based on the yields of "dry bio-oil", CO, and CO_2, the data in Table 33 show that sugarcane bagasse, pretreated energycane, and eucalyptus were the best feedstocks for fast pyrolysis. On the same basis, the worst feedstocks were untreated banagrass followed by pretreated banagrass and leucaena. This ranking system placed untreated energycane in the middle of the grouping. Note that this ranking does not take into account the crop yields for each species. Table 34 displays the elemental analysis results for the dry bio-oil. In the cited study, the water content of the bio-oils was not determined.

The results in Table 34 show the partitioning of carbon, hydrogen, nitrogen, and oxygen in the bio-oils relative to the amount of each element in the feedstock (daf, dry ash free). The overall trends are similar to those observed for dry bio-oil yields. Sugar cane bagasse, pretreated energycane, and eucalyptus have the highest C partitioning (~51−56 wt %), whereas banagrass and pretreated banagrass (~40−44 wt %) defined the lower end of the range. Oxygen partitioning

Table 34. Elemental Analysis Results for the Dry Bio-Oil from Eucalyptus, Leucaena, Sugarcane Bagasse, Energycane, Energycane S3, Banagrass, and Banagrass S3 at a Residence Time of 1.5 s and 450 °C[a]

	C	H	N	O
sample	wt %	wt %	wt %	wt %
eucalyptus	51.0	52.1	117.0	44.1
leucaena	46.3	45.1	109.1	33.6
S-bagasse	56.4	61.3	52.6	52.6
E-cane	50.1	52.3	50.5	42.5
E-cane S3	55.4	59.7	86.8	54.3
banagrass	40.8	43.6	58.3	32.8
banagrass S3	43.6	44.6	103.1	37.6

[a] Presented as wt % of the element in the feedstock (daf). Reproduced from Morgan, T. J.; Turn, S. Q.; Sun, N.; George, A., Fast Pyrolysis of Tropical Biomass Species and Influence of Water Pretreatment on Product Distributions. PLoS ONE 2016, 11, (3), e0151368 (ref 165). Copyright 2016, Creative Commons CC0 public domain dedication. The standard deviation for the C and O results is ≤±3.0 wt %, for H ≤±5.0 wt %, and for N ~±20 wt % (absolute).

followed a similar trend to that of carbon, with bio-oil from sugarcane bagasse and pretreated energycane containing ~50–55 wt % of the feedstock oxygen, with the lowest amounts, 33 wt %, determined for banagrass and leucaena bio-oils. Hydrogen partitioning to bio-oil was greatest for sugarcane bagasse and pretreated energycane (~60 wt %) and lowest for banagrass and pretreated banagrass (~44 wt %). Data for nitrogen are less conclusive due to the small amounts of nitrogen present in the feedstocks which resulted in larger measurement uncertainties. Despite this limitation, there appears to be a greater partitioning of nitrogen to the bio-oils from eucalyptus, leucaena, pretreated banagrass, and pretreated energycane than for the other feedstocks.

Comparison of the untreated and pretreated feedstocks shows that in all cases there is greater partitioning of all elements to the bio-oil from the pretreated samples. The effect appears to be more significant for nitrogen than other elements, but this may be a reflection of the greater uncertainty in the nitrogen results.

Other than the two publication cited above, there are no other reports (to our knowledge) on the fast pyrolysis of *Pennisetum purpureum* species for bio-oil production. Mesa-Perez et al.[316] examined the fast pyrolysis of elephant grass in a 200 kg/h pilot plant for charcoal production, but bio-oil and gas yields were not given. Slow pyrolysis studies of elephant grass have been reported using fixed-bed reactor configurations.[317,318] Braga et al.[319] reported on the slow pyrolysis of elephant grass (*Pennisetum purpureum Schum*) after pretreatment via hot water or acid washing. Washing reduced the ash content from ~7.0 wt % wet basis to ~2.5 wt % and improved the volatiles yield and apparently reduced activation energy. The study was carried out using a thermogravimetric analyzer, and the ash composition was not reported making their findings difficult to interpret.

Two slow pyrolysis studies of napier grass have been reported. Mythili et al.[320] obtained ~26 wt % bio-oil and ~28 wt % char (basis not given) using a fixed bed reactor with a maximum heating rate of 15 °C/min to 450 °C. Lee et al.[321] reported a maximum bio-oil yield of ~35 wt % with ~30 wt % char (basis not given) using a heating rate of 150 °C/min to 500 °C. In both studies, the residence times of volatile products was not reported and it is not clear whether the bio-oil yields include pyrolysis water and/or moisture.

Eucalyptus: Fast pyrolysis studies of eucalyptus have been reported using bench- and lab-scale fluidized bed reactors.[322−325] In general, a high bio-oil yield can be achieved (organic fraction ~50–60 wt % daf, relative to the daf feedstock) with relatively low amounts of char when operating at a reaction temperature of ~500 °C and a residence time of <2 s. Results of eucalyptus grown in Hawai'i[165] are shown in Tables 33 and 34. The bio-oil yield was somewhat lower than reported by other researchers and the char yield slightly greater. These differences are likely due to the lower, 450 °C reaction temperature used[165] compared to other cited studies (~500 °C).[322−325] The results are in general agreement with those performed on other hardwoods.

Pighinelli et al.[326] studied the fast pyrolysis of Brazilian sugarcane trash and *Eucalyptus benthamii*, comparing the effect nitrogen as process gas on product yields vs recycled pyrolysis flue gas (reducing environment). The use of flue gas improved the bio-oil quality in terms of lower oxygen content, total acid number, and viscosity while increasing the heating value. An increase in the amount of aromatics in the bio-oil was also observed when using flue gas; however, the bio-oil yield also decreased by ~13 wt % absolute. Using a nitrogen environment produced a bio-oil yield of ~60 wt % from *E. benthamii* of which 10 wt % absolute was water (~14 wt % char), the sugarcane trash was not examined in N_2. When a flue gas environment was used, the bio-oil yield of *E. benthamii* was 58–64 wt % of which 20–25 wt % (absolute) was water and the associated char yield was 7–8 wt %. Pyrolysis of sugarcane trash under flue gas yielded a bio-oil fraction of ~32 wt % relative to the daf biomass; however, the bio-oil is mostly water (~20 wt % absolute of the 32 wt % bio-oil is water) and a char fraction of ~10 wt % daf biomass.

Rice Husks: A great number of fast pyrolysis studies of rice husks have been reported using various reactor designs. Only studies using fluidized-bed and spouted-bed reactors are discussed herein due to the low pyrolysis oil (bio-oil) yields from fixed-bed reactors. Relatively high yields of bio-oil can be obtained (45–55 wt %); however, the oil has relatively high water content (typically 20–25 wt % absolute) and char yields are high (~20–30 wt %); the char can contain up to 50% ash. Rice husks have very high ash content, which is typically >90% silica. It is possible that high value amorphous silica can be recovered from the char due to the relatively low process temperature used for fast pyrolysis (see citations below).

Ji-lu[327] examined the effect of reaction temperature on bio-oil yields using a lab-scale fluidized-bed reactor. A maximum bio-oil yield of 56 wt % was obtained at 465 °C, and the oil contains ~25 wt % water. Char yields range from 20 to 35 wt % (~25% at 465 °C). The fuel properties for bio-oils produced at various temperature was also reported along with gas composition, oil composition (by GC), and analysis of the energetic performance of thermal conversion.

Heo et al.[328] studied the effects of reaction temperature, flow rate, feed rate, and fluidizing medium (N_2 or recycled process gas) on the fast pyrolysis of rice husks using a bench-scale fluidized-bed reactor. The optimal conditions for maximum bio-oil yield (~60 wt %) were a temperature of 400–450 °C and using recycled process gas as fluidizing medium. High flow rates and feeding rates also improved the oil yield. Under the optimized conditions, the char yield was ~30 wt % and the bio-oil contained ~25 wt % water.

Li et al.[329] examined the use of various bed materials to improve the quality of water-soluble organic products from the fast pyrolysis of rice husks in a lab-scale fluidized-bed reactor. It was demonstrated that the choice of bed material (red brick, calcite, dolomite, or limestone) can significantly alter the composition of the water-soluble organics; refer to the original publication for details.

Alvarez et al.[330] used a bench-scale spouted-bed reactor to produce bio-oil from rice husks over the temperature range of 400–600 °C with a residence time of <2 s. A maximum bio-oil yield of ~70 wt % was achieved at 450 °C with an associated char yield of ~25 wt % (~50% ash content). The water content of the bio-oils were 23–24 wt % in all cases. Fuel properties of the bio-oils and char were also reported.

Meesuk et al.[331] examined the effects of catalyst (in-bed) and gas atmosphere (N_2 vs H_2) on bio-oil yields and composition from rice husk using a bench-scale fluidized bed reactor. The use of catalyst and H_2 resulted in a bio-oil with lower oxygen content than when N_2 was used. The oxygen content ranged from ~31% when no catalyst and N_2 were used to ~10 wt % when $CoMo/Al_2O_3$ catalyst and H_2 were used. The water content of the bio-oils ranged from ~20 wt % when

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no catalyst and N_2 were used to almost 50 wt % when $CoMo/Al_2O_3$ catalyst and H_2 were used.

Cai and Liu[332] reported results from a commercial scale fast pyrolysis reactor (1−3 Mg/h input rice husks) operating at 550 °C. The bio-oil yield was ∼48 wt % with a char yield of ∼30 wt %. The water content of the bio-oil was 33−38 wt %. A detailed account of the operating conditions as well as the fuel properties and composition of the bio-oil and char were presented.

For comparison, Tsai et al.[333] reported product yields and compositions from fast pyrolysis of rice husks using a fixed bed reactor. The maximum bio-oil yield was ∼40 wt % at reaction temperatures of 500 °C or greater; the water content of the oil was not reported.

Rice Straw: Phan et al.[334] assessed the bio-oil production potential for four types of Vietnamese biomass (rice husks, rice straw, sugarcane bagasse, and corn cob) using a fluidized bed fast pyrolysis reactor. The reaction temperature used to compare the feedstocks was 500 °C with a <2 s residence time. Rice straw was examined over a temperature range of 470−515 °C and at various flow rates. Rice straw produced the least amount of bio-oil (∼50 wt %) and the most char (∼30 wt %), rice husk produces slightly more bio-oil (∼55 wt %) and a similar amount of char. Bagasse was the best performing feedstock generating ∼65 wt % bio-oil and <10 wt % char. Water content of the bio-oil from bagasse, rice husks, and rice straw was reported to be ∼17 wt %, ∼22 wt % water, and ∼28 wt %, respectively. Fuel properties and composition determined by GC analysis of the bio-oils were also reported.

Pattiya and Suttibak[335] studied the effect of a glass wool hot vapor filter on bio-oil yield and composition from rice straw and rice husks using a bench-scale fluidized bed reactor. The maximum bio-oil yield for rice straw and rice husk was obtained at ∼400 °C (∼54 wt %) and ∼450 °C (58 wt %), respectively. The water content of the rice straw bio-oil was ∼22 wt % when no hot filter was used and ∼31 wt % when the hot filter was used. The rice husk bio-oil showed similar trends, with a water content of ∼24 wt % without a hot filter and ∼27 wt % when one was used. The use of the hot filter reduced the bio-oil yields by 5−10 wt % (absolute) but produced a better quality oil, probably due to condensation of heavy oil on to the filter. Fuel properties of the bio-oils were also reported.

Li et al.[336] looked at the influence of reaction conditions on the products from the fast pyrolysis of rice husk and rice straw, comparing spouted-bed vs fluidized bed conditions and the effect of red brick as bed material. The maximum bio-oil yields were achieved at a reaction temperature of ∼460 °C for husks (∼48 wt %) and straw (∼53 wt %). The tests using spouted-bed conditions improved the bio-oil yield compared to fluidized-bed conditions. The use of red brick in place of quartz sand reduced bio-oil yield but the oil was of better quality (less oxygen and water, with a higher heating value). Bio-oil composition and fuel properties were also reported.

Lee et al.[337] studied the effect of reaction temperature on bio-oil yield for rice straw using a lab-scale (1 kg/h) fluidized bed reactor. Bio-oil yields of ∼50 wt % and char yields of ∼25−30 wt % were obtained over a temperature range from 412 to 516 °C. The amount of water in the bio-oil was not reported.

Jung et al.[338] obtained a bio-oil yield of ∼65 wt % over a temperature range from 405 to 450 °C using a bench-scale reactor. The bio-oil and aqueous phases separated due to the high water content (>35 wt % absolute daf fuel basis). The associated char yield was ∼20 wt %.

Zhang et al.[339] used a novel lab-scale internally interconnected fluidized bed reactor to study the effect of different catalysts for the production of aromatics and olefins from rice straw. The maximum yields of aromatics (∼13% of feedstock carbon converted to aromatics) and C_2−C_4 olefins (∼10% carbon conversion) were obtained using a ZSM-5 catalyst.

Yang et al.[340] used a bench-scale (1 kg/h) fluidized bed reactor to examine the effect of reaction temperature and flow-rate on the bio-oil yield for rice straw. A maximum bio-oil yield of 41 wt % was achieved at 430 °C. The water content of the oil was not reported. Viscosity and storage stability were also examined.

Sugarcane Bagasse: Montoya et al.[341] evaluated the fast pyrolysis of Colombian sugarcane bagasse as a function of temperature, feed rate, flow rate, and fluidization conditions using a lab-scale fluidized bed reactor (5 kg/h). A maximum bio-oil yield of 73 wt % was obtained at 500 °C with 23 wt % char. The water content of the bio-oil was not reported.

Patel et al.[342] investigated a molybdenum carbide catalyst (in-bed) to improve the quality of bio-oil from sugarcane bagasse using a bench-scale fluidized bed reactor operating at 500 °C. In the absence of catalyst a bio-oil yield of 73 wt % was obtained (dry basis 60 wt %). As the amount of catalyst in the bed was increased, the bio-oil yield decreased from 50 wt % (dry basis) to ∼40 wt % and the water content increased. The bio-oil from catalytic pyrolysis contained significantly less sugars and increased amount of furans and phenols compared to the control.

Numerous other studies on the fast pyrolysis of bagasse have been reported using various reactor designs, catalysts, and reaction conditions. See the studies cited above in the banagrass and rice straw sections for further details of bagasse fast pyrolysis studies (Tables 33 and 34)[165,334] and citations therein. In general, bagasse produces a relatively high bio-oil yield (∼60−70 wt % of the daf feedstock) under fast pyrolysis conditions with an absolute water content of ∼15 wt % (i.e., organic bio-oil yield ∼45−55 wt %). The char yield is dependent on the feedstock particle size, ranging from ∼2 wt % of the daf feedstock to ∼20 wt % with increasing particle size.

Sorghum: The fast pyrolysis of bagasse from sweet sorghum using a fluidized bed reactor has been reported in the literature. Fiber sorghum, however, is the target feedstocks for this study and its use has not been reported in the literature.

Leucaena and Energycane: No publications on these two target crops were identified, other than the study mentioned above under the banagrass subheading.

***Sesbania* and Glyricidia**: No publications were identified.

3.2.3. Hydrothermal Liquefaction (HTL). Reviews of the early work on the liquefaction of coal and biomass have been published by Lowry,[343] M. M. Elliott,[344] and D.C. Elliott.[345] The majority of the early liquefaction work was focused on producing liquid fuels from coal. The findings from those studies provide valuable insights into biomass liquefaction, especially in regard to reactor and process design and the fundamentals of the thermal breakdown of solid fuels in liquid environments. An overview of liquefaction technologies that emerged during the 2 decades following the oil shocks of the 1970s can be found in the "Technology Status Report" by the U.K. Department of Trade and Industry.[346]

Catalysts and reactors for hydroprocessing were reviewed by Furimsky,[347] and Mochida et al.[348] assessed progress in coal liquefaction catalysts in Japan, where a research program on coal liquefaction was maintained far longer than in Europe and the USA. An analysis of costs for various coal liquefaction processes was reported by Sun et al.[349] More recent developments in the hydrothermal processing of biomass have been reviewed by Tekin et al.,[350] Elliott et al.,[351] and several other groups as discussed below. The term catalytic hydrothermolysis (CH) is often used to refer to HTL processing of oils from oil crops as an alternative method for producing HEFA/HRJ; therefore, CH will not be discussed in this section of the review. Only one study was identified that could be considered a form of CH, i.e., the HTL processing of jatropha oil in the presence of a catalyst (see end of section 3.1.1, ref 235). It should be noted that the use of catalysts for the HTL conversion of fiber crops could also be considered a form of catalytic hydrothermolysis which can lead to some confusion with the use of the CH term. In this review, the use of catalysts during HTL conversion of fiber crops is discussed later in this section (those works are NOT referred to as CH herein).

3.2.3.1. Hydrothermal Processing of Biomass. The production of biocrude by the hydrothermal liquefaction (HTL) of lignocellulosic biomass was proposed as replacement for crude-oil as early as 1934 by E. Berl.[352,353] Biomass was processed in an alkaline solution at around 230 °C, and the "oil" product contained ∼60% of the original biomass carbon and ∼75% of its heating value. Most of the early HTL studies used wood feedstocks, but more recently the focus has shifted to agricultural residues, manures, wastewater biosolids, grasses, and algae.[345,351]

This process route has been used to reduce the oxygen content of the substrate and produce liquid and solid products with higher energy densities. Recent efforts have focused on preparing advanced carbon materials. The basic bench scale experiment consists of heating wet biomass plus added water, and any added catalyst, in a batch autoclave where system pressure is allowed to rise with increasing reactor temperature. The process reduces or eliminates the need for a predrying step, which reduces energy consumption. Furthermore, energy losses from the conversion of liquid water to steam are limited by heating the water under the high pressures generated in the closed vessel. For a continuous flow HTL process, the lignocellulosic biomass requires particle size reduction prior to feeding, while some types of algae, manure, and wastewater biosolids are already within the correct size range for direct processing.[351]

Although the ability of HTL to process wet biomass has been considered one of its main benefits, it has been reported that the feeding of wet biomass still remains a significant problem due to issues with plugging.[351] This has led to studies on slurry feeding system; however, depending on the type of biomass, this approach requires the biomass to be significantly sized reduced, which requires feedstock drying (i.e., for woody biomass). More recent work has focusing on wet grinding methods with an aim of reducing costs. For example, sorghum stalks have been processed using wet ball milling to generate a slurry that could be pumped at 21 MPa.[351]

The range of products made by hydrothermal processing may be altered by the selection of reaction conditions. "Char" is the main product when lignocellulosic biomass is heated to 170−250 °C in the presence of a catalyst (e.g., citric acid, $FeSO_4$) for 4−15 h at pressures ranging up to 50 bar.[354] Hydrothermal "*liquefaction*" requires somewhat higher temperatures compared to hydrothermal "*carbonization*". Zhang et al.[355] collected a phenol-rich oily liquid from heating lignocellulosic biomass to between 250 and 350 °C in the presence of K_2CO_3 or KOH, with pressures from 50 to 200 bar and reaction times of 15 min. In these experiments, the liquid phase was deemed to be "near" supercritical water. Note that the critical point of water is 374.15 °C and 221.2 bar. For a starting biomass feedstock containing 30−50 wt % oxygen and 10−20 MJ/kg heating value, oil produced from hydrothermal liquefaction typically has an oxygen content between 10 and 30 wt % and heating values of 30−36 MJ/kg. Thus, while some upgrading is expected, the oxygen content of the "oil" is still high which leads to challenges in its utilization.[351,356−358]

In another "near" supercritical water experiment, somewhat higher temperatures (350−380 °C) were used in the presence of Ru and Ni based catalysts, generating pressures between 180 and 300 bar. Reaction times of less than 1 h at these conditions produced mainly CH_4 and CO_2.[359] "Hydrothermal gasification" is the term used for reaction conditions above the critical point of water that shift the product distribution toward gas phase products.[351,356−358,360] Experiments above the critical point of water (600−700 °C) produce H_2, CH_4, and CO_2, in 15 min, at pressures of 250−300 bar.[361]

Akhtar and Amin[360] reviewed the role of hydrothermal liquefaction process conditions including liquefaction medium, solvent density, temperature, pressure, heating rate, particle size, biomass feedstock, residence time, and gas environment (e.g., reducing gases or hydrogen donors). Short contact (a few minutes) hydrothermal processing experiments with woody and herbaceous biomass at 200−230 °C were shown to extract nearly 100% of the hemicellulose, 4−22% of the cellulose, and 35−60% of the lignin.

It has long been known that the addition of acids and bases can decompose lignocellulosic biomass into monomers.[362−364] The use of bases has been shown to reduce the amount of low molecular weight oxygenates and furans in HTL oils.[345] Typical catalysts for hydrothermal liquefaction are alkalicarbonates and alkalinehydroxides, these catalysts have occasionally been used in the presence of reducing gases such as CO and H_2.[356,357]

A major drawback to the production of jet fuel from the hydrothermal liquefaction of lignocellulosic biomass is that relatively few studies have been carried out to investigate continuous-flow processes that would be required for industrial applications.[351] In a useful review, Elliott[365] discussed early work on continuous-flow process development at Lawrence Berkeley Laboratory by Schaleger et al.,[366] at the Albany Biomass Liquefaction Experimental Facility,[367] as well as later work on the Hydrothermal Upgrading Plant in The Netherlands.[368] The capacities of these units were in the range of 10−100 kg/h.

Two pilot/demonstration start-up companies in Spain and Switzerland have more recently (2015) announced the use of "semi-continuous" hydrothermal *carbonization* processes. Meanwhile, relatively little effort appears to have been made for developing hydrothermal *liquefaction* technologies at pilot- or demonstration-scale.[351,356,357]

Development of hydrothermal processes would benefit from the improved characterization of reaction pathways and of reaction kinetics. Much of the exploratory work to date has made use of closed ("batch") reactors. Elsewhere, evidence has

Table 35. Typical Hydrothermal Processing Conditions and Products[a]

	hydrothermal carbonization	hydrothermal liquefaction	hydrothermal gasification
reaction medium	water (liquid)	water (liquid)	water (near/above supercritical)
typical temperature range	170–250 °C	250–350 °C	350–380 °C/600–700 °C
typical pressure range	10–20 bar(g)	50–200 bar(g)	180–300 bar(g)/250–300 bar(g)
typical catalyst	citric acid or FeSO4	alkalicarbonates, alkalinehydroxides	Ru, Ni, none
typical reaction time	4–16 h	10–15 min	<1 h/1–5 min
main products	char suspension or granulate	phenol rich, oily liquid	hydrogen, carbon dioxide, methane
product separation	filtration and drying	phase separation hydrophobic/hydrophilic	phase separation gaseous/liquid

[a] Reprinted from *Biomass and Bioenergy*, Vol. 35, Heilmann S. M., J. L. R., Sadowsky J. M., Schendel F. J., von Keitz M. G., Valentas, K. J.:, Hydrothermal carbonization of distiller's grains, 2526–2533, Copyright 2011, with permission from Elsevier (ref 374).

Table 36. Summary of HTL Feedstock and Continuous-Flow Reactor Results[a]

feedstock (db)	lignocellulosic	macroalgae	microalgae	manures	sewage sludge
ash	3–8	15–35	7–26	10–20	20–50
H/C (mole ratio)	1.2	1.2	1.6	1.5	1.6
O% mass	35–45	25–40	25–30	35–45	50
N% mass	0.5–3.0	3–7	5–9	3–6	3–8
HHV MJ/kg	12–20	10–20	25–30	10–20	14
size	1–100 000 mm	1–10 000 mm	1–1000 μm	1–10 000 μm	1–100 000 μm
feed formatting required	yes	not all strains	no	no	depending on source
ref	375,376	377	378	376,379	380
BioCrude					
yield, % daf feedstock	35	27	38–64		
energy recovery, %	64	52	60–78		
N%	0.3	3–4	4–8		
O%	12	6–8	5–18		
ref	381,382	383	384,385	NA	NA

[a] Reprinted from *Bioresource Technology*, Vol. 178, Elliott, D. C., Biller, P., Ross, A. B., Schmidt, A. J., Jones, S. B., Hydrothermal liquefaction of biomass: Developments from batch to continuous process, p 147, Copyright 2015 (ref 351). daf, dry ash free. NA, no reference data available. Feed formatting refers to size reduction and drying.

been reviewed that shows "batch" reactors are of little help in characterizing reaction pathways or reaction kinetics during coal liquefaction.[302] The shortcomings of batch reactors have led to the development of an alternative reactor design for liquefaction, which promises to be helpful in clarifying reaction pathways and providing a route for working out the reaction kinetics.[302,369] To our knowledge, this type of reactor has only been used to study coal liquefaction.

At the time of writing, more work also appears needed for developing overall energy balances and economics. Kruse et al.[370] have suggested that the efficiency of liquor recirculation and heat recovery are key factors in improving overall energy efficiency. Elliot et al.[351] highlighted the need to improve the conversion of the aqueous phase (that can contain up to ~40% C) into useful products to improve overall process efficiency and production costs. Developing catalysts able to withstand hydrothermal reaction conditions as well as methods for their recovery and reuse would improve process economics. In addition, novel solids management methods appear to be required, for dealing with the precipitation of inorganic materials which can foul and plug ancillary equipment.[351,356]

In a recent review (2015), Elliott et al.[351] suggested there was significant potential for the commercialization of continuous-flow hydrothermal technologies. Techno-economic analyses (TEA) indicate that hydrothermal processes have economic potential, especially for converting algae or wet biomass/waste feedstocks into bioliquids. Meanwhile, the cost of constructing, operating, and maintaining corrosion resistant, high-pressure, high-temperature reaction vessels, and ancillary equipment remains a challenge to the long-term commercial prospects of HTL processing of biomass. Research focused on making high value advanced carbon materials appears significantly more promising in pursuing the development of thermal hydrocarbonization, against a background of relatively high plant and operating costs.[370−373] Table 35 lists typical hydrothermal processing conditions and products. Table 36 provides a summary of the properties of HTL feedstocks (lignocellulosic, macro- and microalgae, manure, and wastewater biosolids) that have been studied using continuous-flow reactors alongside results from those experiments.

An enduring challenge in developing hydrothermal liquefaction processes remains the character of the bio-oils recovered from these processes. As in the case of pyrolysis tars/oils, these liquids are difficult to handle, process, and analyze. They are corrosive, can form gum, and separate into aqueous and organic phases during storage. They often contain particles of char and/or ash. The viscosity of the organic phase increases with storage time. Problems are also encountered during ignition in engines due to the low volatility of the fuel and the low calorific values due to relatively high oxygen contents: up to 50% for pyrolysis oils and 10–20% for hydrothermal bio-oils.[300,309,356,357,386−389]

Bio-oils from HTL of biomass tend to separate into aqueous and organic phases. Only the organic phase of the oil is typically upgraded via deoxygenation to produce transportation fuels (gasoline, jet fuel, diesel). For HTL to be viable for commercial scale production of jet fuel, a use has to be found for the aqueous phase of the oil. The yields are otherwise too low, roughly equivalent to those obtained from dry pyrolysis of biomass (fast pyrolysis) where only the organic fraction of the pyrolysis oil is upgraded.

On the other hand, it should be noted that biomass HTL oils contain less oxygen than the organic fraction of fast pyrolysis oils and have a greater energy density, but yields tend to be lower. Phenols are often the major compounds in biomass HTL oils but are present at lower concentration than in fast pyrolysis oils. It has also been shown that wood HTL oils are more aromatic in character than other types of biomass (algae, water hyacinth, kelp, grasses, and manure).[345] The nitrogen content of biomass HTL oils increases in relation to the nitrogen content of the feedstock.[345]

A key aspect of HTL is the availability of a sufficient supply of hydrogen-donor solvent which serves to quench reactive free radicals and chemically stabilize extract molecules. Alternatively, depolymerized material may be dissolved in a suitable solvent and carried away from the parent particle. In a batch reactor and using a relatively small amount of nondonor (albeit powerful) solvent, repolymerization reactions have been identified by observing increased char residues at higher temperatures and longer residence times.[302]

When the sample is heated in an inert gas atmosphere, "dry" pyrolysis allows greater extents of repolymerization and the formation of larger proportions of secondary char residues.[302] The outcome is similar when coals are heated in an inert liquid phase environments, such as extraction in hexadecane. The mass transfer step at the solid−fluid boundary appears to have a critical role to play. As in the case of pyrolysis experiments, the outcome of a liquefaction experiment is dependent on the chemical species involved, the configuration of the reaction vessel, and the nature as well as the relative abundance of the liquid medium.

To arrive at appropriate mathematical models for these processes, it is necessary to identify the key variables and the rate-determining steps. The conceptual modeling of liquefaction depends on the type of experiment being performed.[302] The configurations of batch reactors do not allow tracking reaction sequences or working out reaction kinetics for either coal liquefaction or the hydrothermal processing of biomass. The design of a liquefaction reactor has been described that can facilitate the mathematical formulation of liquefaction processes.[302,369]

In the above-mentioned studies,[302,369] the liquefaction process was defined and modeled in terms of a two-stage process. The resulting calculations gave different energies of activation for the two successive stages, providing justification of the approach. The magnitude of the energies of activation for the "extraction" phase are close to those associated with diffusion, whereas energies of activation for the "depolymerization" stage are closer to values associated with covalent bond rupture. There appear to be clear points of correspondence between the model and the actual physical and chemical processes observed to be taking place during liquefaction.[302,369] To our knowledge, no such studies on the continuous HTL of biomass have been reported where activation energies of the extraction and depolymerization have been derived.

Biomass Liquefaction in Organic Solvents—Overview: Liquefaction of biomass with methanol, ethanol, and acetone has been examined under supercritical conditions (270−310 °C), with and without the use of catalysts.[390] In the absence of catalyst, the largest liquids yields were observed in acetone, with conversions increasing as a function of temperature from 50 to 64 wt %. The use of NaOH and $FeCl_3$ as catalysts was tested. When using NaOH, larger liquids yields were obtained when ethanol or methanol were used as solvent,and decreased when acetone was used, probably due to the poor solubility of NaOH in acetone. With $FeCl_3$ as catalyst, liquid yields up to 72% were obtained in acetone. In all cases, $FeCl_3$ was found to be a more effective catalyst than NaOH.

The use of organic solvents, and in particular hydrogen donor solvents such as tetralin, is known to improve the light oil yield and reduce char formation.[391] However, the data are *not* available to determine whether the use of exotic catalysts and organic solvent is viable for commercial scale processes. These types of process are still in the research phases, and no studies have been reported for processes operating at significant scales and no TEAs have been reported. Therefore, the use of organic solvents for HTL of biomass will not be discussed further.

HTL Lignocellulosic Biomass: In 2010, the National Advanced Biofuels Consortium (NABC[381]) was set up in the U.S. to study processes capable of producing drop-in fuels from biomass. As part of that study, HTL of loblolly pine and corn stover were examined. The findings from that study have been summarized as follows (reproduced from ref 351): (i) The only feed preparation required was size reduction for slurry preparation. (ii) A reducing gas environment was not required. (iii) Water recycling improved biocrude quality and carbon yields and reduced water use and wastewater disposal. (iv) Biocrude was stable (less than 2% change in viscosity after aging at 353 K for 24 h). (v) Reduced reaction severity led to lower quality biocrude. (vi) Overall carbon yield, including hydrotreatment of the biocrude product, was nearly 50%, with the resulting product exhibiting a large fraction in the distillate range. The fate of the carbon in the overall process is summarized in the following paragraph. (vii) These results are based on lignocellulosic feedstocks, and the results could be significantly different for other biomasses, such as algae, with higher nitrogen contents.

Carbon and Mass Balance HTL Lignocellulosic Biomass: The NABC study on HTL of lignocellulosic biomass used a small-scale, continuous-flow reactor to generate approximate mass and carbon balances.[351,381] In total, 100 g of daf biomass produced 47 g of aqueous products containing 37% of the feedstock carbon, 5 g of solids (C unreported), 16 g of gas (C unreported), and 32 g of biocrude that contained 51% of the feedstock carbon. Upgrading required 1 g of H_2 for 32 g of biocrude, producing 1.3 g of gas (C unreported) and 4 g of water. The amount of upgraded final product was not reported, but by difference the amount is ∼27.5 g. When considering the economic value and quality of the products from HTL, optimization of the upgrading process is the main factor.[351]

3.2.3.2. Techno-Economic Analysis of HTL Lignocellulosic Biomass.

Zhu et al.[392] have studied the economics of producing drop-in liquid fuels (gasoline, diesel) from lignocellulosic biomass via HTL and hydrotreatment. The biomass was identified as pine forest residues including bark, but no fuel properties were provided. Mass and energy balances from bench scale HTL experiments with woody biomass were scaled up to commercial scale (2000 dry metric tons/day). Results were also generated for an idealized case to estimate how costs may be reduced in the future; those aspects of the results are not discussed herein.

The design case included feedstock preparation, plug-flow HTL reactor, upgrading (hydrotreating and hydrocracking), and a hydrogen plant.[392] Woody biomass (50 wt % moisture, ground to fine particles) mixed with hot water to produce a slurry (15 wt % dry biomass) was pumped into the HTL reactor at 0.6 MPa. The biocrude separated into two phases. The organic phase was upgraded while most of the aqueous phase (~80%) was recycled to the feedstock preparation step, and the remainder was treated as wastewater. Anaerobic digestion was assumed to be a suitable wastewater treatment, and the product CH_4 was steam reformed to produce H_2 used to upgrade the biocrude. The gas phase from HTL and supplemental natural gas were also steam reformed to produce sufficient hydrogen for upgrading.

The system design sent the heavy fraction of the biocrude to be hydrocracked to produce more gasoline and diesel, although this has yet to be demonstrated experimentally.[392] The off gas from the hydrotreater was sent to a pressure swing absorption system where 80% of the hydrogen was recovered. The tail gas is directed to the steam reformer to produce more hydrogen. The carbon balance for the process is depicted in Figure 23. The main inputs and assumptions used in the study are presented in Table 37.

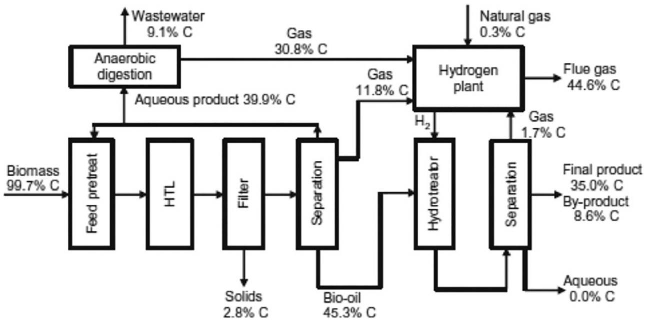

Figure 23. Carbon balance of the HTL process. Reprinted from *Applied Energy*, Vol. 129, Zhu, Y.; Biddy, M. J.; Jones, S. B.; Elliott, D. C.; Schmidt, A. J., Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction (HTL) and upgrading. pp 384–394, Copyright 2014, with permission from Elsevier (ref 392).

Table 37. Major Inputs and Assumptions for the Biomass HTL and Upgrading System[a]

biomass feed rate, dry metric tons/day	2000
dry biomass wt% in biomass-water slurry	15
Hydrothermal Liquefaction	
temperature °C	355
pressure, MPa	20.3
biomass conversion, %	99.9
LHSV, h^{-1}	4
Yields, kg/100 kg dry wood	
bio-oil (biocrude)	29.4
gas	17.8
water (with dissolved organics)	49.7
solid waste	3.0
Gas Composition, wt %	
CO_2	88.3
H_2	0.9
CH_4	1.8
other hydrocarbons	9.0
Water Composition, wt %	
H_2O	67.2
dissolved organics	32.8
Hydrotreating Two Stage Fixed Bed	
temperature, °C (inlet)	165
pressure, MPa (inlet)	13.5
LHSV, h^{-1}	0.54 (stage 1) 0.18 stage 2)
H_2 consumption, g H_2/g dry bio-oil	0.033
Product Distribution, wt %	
deoxygenated oil	81.7
water	15.7
gas	2.5
Deoxygenated Oil Distillation Streams, wt %	
light hydrocarbons (C4)	0.8
gasoline (C5–C10)	41.3
diesel (C10–400 °C boiling point)	39.6
heavy oil (>400 °C)	18.4
Hydrocracking	
temperature, °C (inlet)	n/a
pressure, MPa (inlet)	n/a
LHSV, h^{-1}	n/a

[a] Reprinted from *Applied Energy*, Vol. 129, Zhu, Y.; Biddy, M. J.; Jones, S. B.; Elliott, D. C.; Schmidt, A. J., Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction (HTL) and upgrading. pp 384–394, Copyright 2014, with permission from Elsevier (ref 392).

Zhu et al.[392] found that upgrading bio-oil from HTL of wood produced mainly C_4–C_{17} compounds accounting for ~35% of the carbon, and the overall carbon efficiency was ~44% (including fuel gas and heavy oil). The aqueous phase of the biocrude contained ~40% of the carbon. This highlights the importance of developing methods to convert the carbon in the aqueous phase to useful products.

Economic Evaluation: The cost to produce drop-in fuels was calculated as the minimum fuel selling price (MFSP) in \$/L and as \$ per gallon of gasoline equivalent (\$GGE).[392] The gate price for the feedstock was assumed to be \$70/Mg (in 2007 \$). The results from the cost analysis are listed in Table 38. The two most expensive steps in the entire process are the HTL and hydrotreating reactors which account for ~60% of the cost. The capital cost is higher for HTL than fast pyrolysis or gasification. In addition, no commercial scale HTL plants have been built; therefore, price estimates are uncertain.

The cost analysis shows that the MFSP of the upgraded products is ~4.5 to 5.0 \$/gallon depending on the basis used. This is considerably higher than the range of wholesale gasoline prices in the U.S. between 2007 and 2012 (\$1.77 to 2.93/gallon).[392]

In the same TEA, a distributed HTL route was also examined.[392] In this scenario, a number of smaller scale HTL reactors are distributed throughout an area with the biocrude transported to an existing refinery for upgrading, thus eliminating the need for the hydrotreater, hydrocracker, and steam reformer and their associated costs. Production costs were investigated for different scales of distributed HTL facilities, varying from 10 to 2000 Mg/day dry woody biomass input. In this scenario, HTL facilities larger than 200 Mg/day dry biomass input were able to produce bio-oil at a price competitive with conventional petroleum fuels. Assuming that smaller scale HTL facilities had feedstock prices 50% lower than the centralized case (due to reduced transportation cost,

Table 38. Cost Results for the Woody Biomass HTL and Upgrading System[a]

cost basis 2007 U.S. $	$ million
Installed Costs:	
biomass conditioning	27.8
HTL reactor	88.7
upgrading (hydrotreating)	95.9
upgrading (hydrocracking)	n/a
hydrogen plant	23.8
utilities	37.3
missing equipment	27.4
total installed costs (TIC)	301
indirect costs	187
fixed capital investment (FCI)	488
total capital investment (TCI)	512
operating cost, $ million/year	
feedstock	46
natural gas	0.26
catalysts and chemicals	5.48
waste disposal	25
electricity and other utilities	7.48
coproduct credits	−7.97
fixed costs	23.9
capital depreciation	24.4
average income tax	16.3
average return on investment	45.4
MFSP, $/L product ($/gallon)	1.29 (4.89)
MFSP, $/GGE product	4.44

[a] Reprinted from *Applied Energy*, Vol. 129, Zhu, Y.; Biddy, M. J.; Jones, S. B.; Elliott, D. C.; Schmidt, A. J., Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction (HTL) and upgrading. pp 384−394, Copyright 2014, with permission from Elsevier (ref 392).

etc.) lowered the unit size required for viability to 150 Mg/day.[392]

3.2.3.3. Summary of HTL Process Routes. HTL of woody biomass to liquid fuels (gasoline to diesel range) is technically feasible, but production costs are high in comparison to petroleum based fuels or biomass fast pyrolysis or gasification. The key aspect to reducing costs of the HTL route is to improve the recovery of products from the aqueous phase. Small scale distributed HTL facilities are also feasible; however, this is highly dependent on local conditions, feedstock availability, feedstock costs, transportation costs, and existing refinery infrastructure (hydrotreater, hydrocracker, steam reformer). Based on the data available, it is apparent that liquid fuels produced from HTL of woody biomass is *not* economically competitive with petroleum derived fuels. In addition, costs are higher and the technology readiness is lower than alternative woody biomass to liquid fuels process routes, such as fast pyrolysis and gasification-FT.

Due to the lack of information on continuous-flow processes for biomass HTL or for processes operating at significant scales, it is not possible to identify a reactor type best suited to the production of jet fuel. Knorr et al.[393] compared the economics of five types of HTL reactors. Recent HTL research has focused on developing scalable plug-flow reactors instead of continuous stirred-tank reactors with an aim of reducing capital costs.[351]

Strengths and Weakness of HTL: The potential benefits and drawbacks for a generic (nonspecific) hydrothermal liquefaction process are listed in Table 39.

3.2.3.4. HTL of Tropical Biomass Species. There is a lack of information on mass and energy balances for biomass HTL processes operating at meaningful scales and virtually no information for tropical biomass feedstocks. The information presented in this subsection is from experiments performed using bench- or lab-scale reactors.

Tropical Woody Biomass: There is limited information in the open literature regarding the HTL of woody biomass even though these feedstocks have received greater attention than other types of biomass. Most studies were performed at the bench scale (<1 L reactor volume) using batch reactors to process nontropical feedstocks.[351] Results from these types of test are not a reliable way to derive mass and energy balance for a commercial scale process due to significant changes in product yields and energy efficiencies as the scale changes; also it is highly unlikely that a commercial scale operation would use a batch process.

A single publication on the HTL of tropical woody biomass (eucalyptus and leucaena) was identified. Li et al.[391] examined the effects of mild alkali pretreatment on the HTL of eucalyptus woodchips and the effect of a hydrogen donor solvent (HDS, tetralin) on conversion. When water was used as the HTL solvent, conversion to biocrude was ~60 wt %, and in the presence of a HDS (tetralin), yields approaching 90 wt % were achieved. It was found that using a mixture of HDS and water gave the greatest yields (90 wt % conversion) at less extreme reaction conditions compared to pure tetralin or pure water.[391] While this is a very interesting and useful study from a research point of view, it is not helpful in determining mass

Table 39. Summary of the Strengths and Weakness of Biomass Hydrothermal Liquefaction for the Production of Jet Fuel

strengths	weaknesses
• processing of wet biomass or waste (eliminates need for drying)	• unknown or largely uncharacterized reaction pathways and kinetics
• minimal feedstock preparation (often only size reduction is required)	• inadequate catalysts which do not withstand hydrothermal conditions
• potential for high throughputs	• inadequate solid management practices
• potential for high energy efficiency	• fouling and plugging issues
• potential for high separation efficiency	• biocrude phase separation
• ability to use mixed feedstocks like wastes and lignocellulose	• no demonstrated use for the aqueous phase
• production of direct replacements for existing fuels	• specialized materials required to withstand high temperature, high-pressure, and often corrosive environments
• no need to maintain specialized microbial cultures or enzymes	• no experience at commercial scale
	• low yields
	• high costs

or energy balances or costs related to the commercial scale processing of tropical woody biomass species.

For context, HTL of loblolly pine (nontropical wood) using a small scale continuous-flow reactor yielded ~31% biocrude, which contained ~50% of the carbon in the daf feedstock.[351,381] A biocrude yield of ~30 wt % appears to be fairly typical for woody biomass with the current state of technology.

After reviewing the literature, it is apparent that further research is required to understand how tropical woody biomass species (such as eucalyptus and leucaena) behave during HTL processing. Work is required to optimize process conditions for woody biomass species in general and in particular for tropical species (pretreatment method, reaction temperature, reaction time, HTL solvent, particle size, feeding mechanism, catalyst, etc.).

Tropical Grasses and Agricultural Residues: In general, there is a lack of information on the HTL of rice straw, rice husks, banagrass, sugarcane bagasse, energycane, sesbania, and glyricidia (gliricidia).

Rice is probably the single largest crop grown in tropical regions. Many studies have been undertaken to try and find an economically viable route for processing its byproducts (straw and husks/hulls). However, only a few publications on the HTL of rice straw or husks have been reported.

Rice Straw: Singh et al.[394] investigated the effect of the gas environment on the conversion of rice straw to biocrude. Small scale tests (500 mL) performed in a batch reactor found that using oxygen instead of nitrogen in the reactor significantly reduced the oil yield. In all cases, the biocrude yields and feedstock conversions were low, ≤17 wt % and ~78%, respectively, when operating in a nitrogen atmosphere. The aqueous phase was the main product (>50 wt %) in all the tests. Greater biocrude yields (up to ~31 wt %) from rice straw have been achieved using organic solvents instead of water, see refs 394 and 395 for more information and references cited therein.

Ying et al.[396] studied the hydrothermal liquefaction and carbonization of rice straw and water hyacinth. HTL was performed in a batch reactor (500 mL) using water as solvent with no catalyst at a temperature of 300 °C and residence time of 30 min. The biocrude yields were ~22 wt % for rice straw and ~12 wt % for water hyacinth. The main components of the biocrude were phenols followed by acids for rice straw and acids followed by phenols for water hyacinth.

Lyu et al.[397] examined a novel nanofiltration process for recovering high-value chemicals from the HTL of rice straw; while this is interesting from a research prospective, it is not directly relevant to the commercial scale production of jet fuel. Of interest however was the fact that the biocrude used in the nanofiltration study was produced in an 80 L pilot scale reactor owned by Shanghai Fuhuan Bioenergy Co. Ltd. Detailed information on the reactor design, the pilot plant, product yields, and product qualities (chemical composition, stability, etc.) were not provided.

Rice Husks: Fewer studies have been reported for the HTL of rice husks than for rice straw. Shi et al.[398] examined the HTL of rice husks in a 10 mL batch reactor to study the effect of metallic oxide catalyst on biocrude yields. When no catalyst was used, biocrude yields of 12−24 wt % were obtained. The use of La_2O_3 catalyst increased yields to a maximum of ~33 wt %. The metallic oxide catalysts also improved the quality of the biocrude by reducing oxygen content and increasing its heating value.

The HTL of rice husks in ethanol was studied in a lab scale batch reactor by Hadi et al.[399] The effect of temperature and residence time at temperature was examined. A maximum biocrude yield of 69 wt % was obtained at 325 °C and 30 min reaction time. The resulting biocrude contained ~18 wt % water and had a heating value of ~15 MJ/kg. The biocrude yield appears to be high in comparison to other reports and other feedstocks. It is not clear how the authors determined what proportion of the biocrude was from the rice husks and which are reaction products from ethanol.

Only two other studies on the HTL of rice husks have been reported for the production of biocrude;[400,401] however, those studies did not investigate the effects of reaction conditions on product yields or analyze the biocrude quality. A maximum biocrude yield of ~9 wt % was reported.

A more promising avenue for the exploitation of rice husks may be hydrothermal carbonization to produce biochars for water treatment. A number of studies have shown that the biochar byproduct from HTL of rice husks have novel properties compared to other types of biochar (such as from pyrolysis or gasification) making them suitable for lead removal from water;[402] also see references therein.

It is worth noting that rice husks are widely used as feedstock in biomass combustion plants, most notably in California, India, and throughout Asia, typically operating at a scale of 10−20 MW_{th} input. From a personal discussion with the chief operating officer of a 15 MWth biomass combustion plant under construction in the Philippines (August 2016), the price of rice husks has risen to a point where it is no longer a viable feedstock for the project. Planning is underway to use Napier grass as a replacement fuel.[403]

Banagrass: Pennisetum is a genus that includes napier and elephant grasses. Banagrass is *Pennisetum purpureum* and pearl millet is *Pennisetum glaucum*. Crosses of banagrass with pearl millet have been introduced into Hawai'i, and exact differentiation between many of the giant grasses are difficult without genetic examination. Only one reference was identified for the HTL of Napier grass. Elliot et al.[345] used a 1 L batch reactor with sodium carbonate as a catalyst with an over pressure of CO (~50 bar). Experiments were conducted at 350 °C with a residence time of 30 min (in addition to a 30 min heat up period). Napier grass yielded an oil that was 34.4 wt % of the daf feedstock with carbon and oxygen contents of ~75% and 17%, respectively. This compares to oil yields of 34.7 wt % for spent distillers grain, 26.6 wt % for sorghum, 26.0 wt % for water hyacinth, and 19.2 wt % for kelp processed under the same conditions. Phenols were the major component of the HTL oils accounting for 30−45 wt % of the GC range material. Based on these results, Napier grass (hence also banagrass, elephant grass, and others in the *Pennisetum* genus) has potential as a HTL feedstock when compared to the other feedstocks examined in that study. For context, biocrude (bio-oil) yields from HTL of woody biomass are typically ~30 wt %.[351]

Sorghum: Elliot et al.[345] examined the HTL of sorghum under the conditions described above for banagrass. The oil yield was 26.6 wt % with a carbon content of ~76% and an oxygen content of ~14%. No other publication could be identified for the production of liquid fuels (gasoline to diesel) from sorghum. Most of the research on sorghum is aimed at ethanol production via fermentation or the production of chemicals, such as citric acid or vinegar.

Sugarcane Bagasse: A great number of liquefaction studies have been published on bagasse. However, the vast majority of these studies focus on the production of ethanol or chemicals via HTL-hydrolysis or HTL in organic solvents (with or without catalyst). Many studies have also examined the coprocessing of bagasse with coal or lignin isolated from bagasse (i.e., in relation to ethanol production where lignin is a waste product).

Only one publication was identified for the production of biocrude from HTL of bagasse.[404] In this study a 1 L batch reactor was used to examine the effect of the HTL solvent on biocrude yield and quality, comparing water with tetralin (hydrogen donor) and mixtures of water and tetralin. When water was used as solvent, the maximum biocrude yield was ∼67 wt % and in tetralin ∼84 wt %. Using a mixture of water and tetralin gave the greatest yields (∼88 wt %) and produced a biocrude with lower oxygen content (∼16−20 wt % O) and the greater heating value (32−35 MJ/kg) than when pure water or pure tetralin were used. No information could be found regarding mass or energy balances or production cost.

Based on the above results,[404] bagasse appears to be a very good candidate feedstock for biocrude production via HTL. Yields of ∼67 wt % biocrude reported when using water as solvent clearly exceed the maximum yield of ∼30 wt % for woody biomass and many other feedstocks as detailed in the previous sections. It is not clear, however, if the 67 wt % yield for bagasse included water which may account for the unusually high yield. Results from HTL tests that used organic solvents should be viewed with caution as the solvent can often react and form compounds that partition to the biocrude, giving artificially high yields and conversion rates.

Energycane, Sesbania, and Glyricidia (gliricidia): No publications were identified.

Summary of HTL of Tropical Biomass: There is limited information available from the open literature regarding the conversion of tropical woods, grasses, or agricultural residues into liquid fuels via HTL. Rice straw and sugarcane bagasse have been more widely studied than the other species of interest to this study. In all but a few cases, however, these are early stage studies often focused on products other than transportation fuels. No detailed information is available regarding mass or energy balances, or production costs, for any of the tropical biomass species of interest in this review.

3.2.4. Sugar Crop Process Routes. Biomass with high sugar or starch contents, or sugars generated from cellulose and hemicellulose via hydrolysis, can be converted to jet fuel using processes known as Direct Sugars to Hydrocarbons (DSHC) or Alcohol to Jet (ATJ). In this review the focus is placed on (i) the production of sugars via hydrolysis of lignocellulosic biomass and (ii) the production of alcohols via methods other than fermentation of sugars. The technical aspects of DSCH and ATJ methods will only be briefly discussed.

3.2.4.1. Sugars Production. Sugars can be directly extracted from food crops high in sugars and starch such as sugarcane, corn, sweet sorghum, sugar beets, cassava, etc., which are typically referred to as first generation feedstocks. Due to competition with food there is interest in producing fermentable sugars from lignocelluosic biomass, agricultural residues, and MSW, which are referred to as second generation feedstocks. Any biomass material can be processed to release hexose from cellulose and pentose from the hemicellulose. Reviews on the production of alternative jet fuels from advanced sugar fermentation technologies can be found elsewhere.[229,405]

The use of sugarcane juice for the production of sugar and its conversion to ethanol is *not* discussed in this review due to the abundance of information available on the subject. Refer to the following references for details (refs 262 and 406) and citations therein. This report focuses on the production of sugars from second generation feedstocks (lignocellulosic biomass) via hydrolysis. Once fermentable sugars are produced they can then be converted to alcohols or to hydrocarbons by a number of different biochemical and/or thermochemical pathways. What follows is a brief description of some of the processes. This is followed by an overview of methods for producing alcohols excluding approaches based on the fermentation of sugars.

Sugars are typically produced from second generation feedstocks using enzymatic or acid hydrolysis where the cellulose and hemicellulose are converted in C_5 and C_6 sugars (also referred to as reducing sugars, fermentable sugars, or pentose and hexose). These processes have their limitations. Acid hydrolysis uses a homogeneous liquid acid catalyst which cannot be easily recycled, uses acids at elevated temperature that can lead to breakdown of sugars, requires significant energy input, and generates large amounts of acidic effluent which is difficult to treat.[407,408] Enzymatic hydrolysis suffers from high enzyme costs and low enzyme activity.[408,409] Enzymes, produced by living organisms to catalyze biochemical reactions, also present challenges related to maintaining catalytic activity.

It has been noted that the use of wood based feedstocks has advantages over corn-based feedstocks.[410] For hydrolysis of lignocellulosic materials to be effective, a pretreatment is required to improve access to the cellulose and hemicellulose by removing lignin and other physical barriers. Physical and chemical methods can be used to expose and partially degrade the cellulose and hemicellulose. A great number of pretreatment methods have been researched as have numerous types of enzymes and catalysts to improve hydrolysis yields. It is beyond the scope of this review to cover all the possible routes; refer to Khoo[411] for a review of 55 types of pretreatment and hydrolysis pathways and also see refs 410 and 412.

One of the issues with the hydrolysis method is that the sugars from hemicellulose (often referred to as C5 sugars or the pentose fraction) are more difficult to produce and to ferment. Therefore, it is more difficult to hydrolyze hardwoods than softwoods due to their greater hemicellulose content.[410] Olcay et al.[413] reported experimental results for the production of jet fuel from C5 sugars from hemicellulose. The first step converts xylose from hemicellulose to furfural via dehydrated (in their study pure furfural was used rather than hemicellulose). Furfural is reacted with acetone (NaOH catalyst) using aldol condensation and Michael addition. Hydrocycloaddition of the intermediates is used to produce C13 oligimers and larger compounds using Diels−Alder reactions. The final step is hydrodeoxygenation to generate liquid alkanes (including branched alkanes).

Once sugars are produced they can be converted to alcohols by well documented fermentation based methods (not discussed herein). An alternative approach is to directly convert the sugars into hydrocarbons (direct sugars to hydrocarbons, DSHC) by chemical, thermochemical, or biochemical methods.[223,231] The products can be used as "drop-in" replacements for transportation fuels (gasoline to

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diesel). The best known example is Virent's patented BioForming process that has been described by Blommel et al.[406] and is summarized below.

The feedstock for DSHC processes can be lignocelluosic materials, sugars, or starches. A key aspect of Virent's process is the ability to utilize sugars from hemicellulose and cellulose via catalytic hydrotreatment and the ability to process streams containing many types of water-soluble carbohydrates. The intermediate products (polysaccharides, C5 and C6 sugars, furans, phenolics, and acids) can be converted to alkanes and aromatics using aqueous phase reforming (APR); gasoline, diesel, jet fuel, hydrogen, alcohols, and other oxygenated compounds can be produced. The most significant aspect of the process is APR, which uses proprietary heterogeneous catalysts and a variety of processing conditions to tailor products to specific applications (transport fuels or chemicals).

Blommel et al.[406] reported an economic assessment of Virent's BioFroming process using sugarcane as feedstock ($17 per Mg) to produce liquid fuels (gasoline to jet fuel) assuming 85% conversion of sucrose to liquid fuels. It was shown that the production costs were comparable to prices of fossil derived liquid fuels and ethanol from sugarcane. The main cost drivers are feedstock cost and capital recovery. In addition, if the hemicellulose and cellulose present in the resulting bagasse were hydrolyzed and processed using Virent's technology, the yield of gasoline could be increased by 30%. The use of bagasse would require additional equipment and have a higher liquid fuel production costs. Virent's process was reported to be cost competitive with liquid fuels derived from petroleum when a barrel of crude costs >$60. Mass and energy balances were not reported.

Another DSHC approach uses genetically modified microorganisms that can ferment sugars into hydrocarbons. One such approach produces farnasene, which can then be hydrotreated to produce farnasane, which can be blended with conventional jet fuel or further upgraded to jet fuel range compounds. However, no detailed information about these methods were identified which may be due to the propriety nature of the research and attempts to commercial these processes by companies such as Amyris and LS9. For further details refer to the following reviews and citations therein (refs 223 and 231).

Bond et al.[414] reported experimental results and a TEA for the production of jet fuel range alkanes from C_5 and C_6 sugars from hardwood (red maple). The processes involves pretreatment, hydrolysis, and dehydration to produce furfural and levulinic acid. Catalytic aqueous phase upgrading is used to produce a mixture of linear, branched, and cyclic alkanes. The residue lignin was processed using catalytic fast pyrolysis (in bed) to determine if this was a viable option to increase product yields. However, the yield of useful products from pyrolysis was low (char was the main product), and combustion of the lignin to generate power and heat was considered to be a more viable option. Carbon conversion for hemicellulose sugars to alkanes is ~80% and for cellulose ~50%. An MSP of $4.75/gallon was calculated based on an *n*th commercial plant producing 38 million gallons/year liquid fuels.

Wang et al.[415] demonstrated a catalytic HTL process for converting glucose, sorbitol, and a xylitol/sorbitol mixture (representative of plant derived sugars) to liquid fuel with ~32% yield. The liquid contains ~70% aromatics and napthenes; the remainder consists of alkanes and oxygenates. The reaction was carried out in a bench scale continuous flow reactor using a Ni-HZSM-5 catalyst at 280 °C, 4 MPa hydrogen, WHSV 1.25 h^{-1}, and GHSV of 2500 h^{-1}. The ability to produce aromatics is key to developing renewable jet fuels as they constitute up to 30% of conventional jet fuel, and current renewable processes can only produce alkanes.

Due to the propriety nature of most of the steps developed for DSHC processes, there is limited information in the public domain. In addition, it is difficult to identify relevant literature as most publications focus on individual steps in the DSHC process, often using model compounds to understand specific reaction mechanisms rather than reporting results from the processing of biomass to jet fuel range compounds.

Mass Balances: The yields of sugars (intermediate) and jet fuel (final product) have been summarized for various feedstocks by Wang and Tao;[223] the yields were reported in gallons of gasoline equivalent per dry mega gram (tonne) of feedstock (GGE/Mg). Sugar yields range from ~55 GGE/dry Mg sugar beet to ~92 GGE/dry Mg corn stover; sugarcane bagasse and hardwood yields are ~63 and 75 GGE/dry Mg, respectively.[223] In terms of jet fuel yields, the range is from ~21 to 59 GGE/dry Mg (~18 to 53 gal/dry Mg) where the lowest and highest values are for corn stover assuming different conversion pathways from sugars to jet fuel. The jet fuel yields from the catalytic upgrading of sugars from sugarcane bagasse and hardwood are ~49 and ~42 gal/dry Mg, respectively.[223]

Production Costs: There is limited information on the production costs of jet fuel range hydrocarbons from sugars. The production cost estimates for catalytically upgrading sugars to 2,5-dimethyl furan and 5-hydroxymethylfuran (representative of intermediates that can be converted to jet fuel) range from 6.2 to 9.4 $/gallon.[223] Information on the production cost of jet fuel via this route was not identified. The production cost of the biological route for conversion of sugars to the intermediate pentadecane is ~4.6 $/gallon, with further conversion to jet fuel estimated as ~7.2 $/gallon.[223]

Strengths and Weakness of DSHC Processes: The strengths and weaknesses of DSHC processes (for catalytic and microbial routes) are summarized in Table 40. The main weaknesses are related to a lack of information in the open literature.

3.2.4.2. Hydrolysis Derived Sugars from Tropical Biomass. **Sugar Bagasse**: There is a large amount literature on the production of fermentable sugars from sugarcane bagasse via enzymatic and acid-catalyzed hydrolysis as well as various

Table 40. Summary of the Strengths and Weakness of Sugar to Hydrocarbon Processes

strengths	weaknesses
• feedstock flexibility	• limited information for reaction pathways and kinetics for the entire process
• high specificity for jet fuel range compounds	• catalysts are under development (for catalytic pathways)
• potential for high-energy efficiency	• need to maintain specialized microbial cultures (for biochemical pathways)
	• no experience at commercial scale
	• yields are not available from the open literature
	• energy efficiency of the entire process is not available from the open literature
	• costs are largely unknown
	• more feedstocks need to be studied

pretreatment methods dating back to at least the 1970s. A brief review of past and present research follows.

Jones and Yang[416] studied the kinetics of the simultaneous enzymatic hydrolysis of cellulose and sucrose from bagasse using cellulase and invertase in 1980. It was also demonstrated that the use of a continuous flow reactor design in combination with a hollow-fiber ultrafiltration membrane was effective at removing inhibitory products from the reaction medium, leading to improved yields of reducing sugar.

Verardi et al.[417] compared two impregnating agents for the steam explosion pretreatment of sugarcane bagasse prior to enzymatic hydrolysis to improve fermentable sugar yields. Both impregnation agents were effective at increasing yields by decreasing the amount of inhibitor compounds generated during steam explosion. The authors concluded that this approach can lead to greater efficiency of ethanol production via fermentation, reduced energy requirements, and lower environmental impacts.

Ghosh et al.[418] suggested an integrated biorefinery approach to the production of fuels and chemicals from bagasse that could be integrated with existing sugar mills. The experimental study was aimed at overcoming the lack of implementation of existing cogeneration technologies due to high costs and technical risks. Acid hydrolysis and enzymatic saccharification were used to produce glucose and xylose from the bagasse. Furfural was produced from the pentose fraction with electricity production from the lignin. Under optimized conditions, 366 mL of ethanol were produced from 1 kg of bagasse as well as 149 g of furfural and 0.30 kWh electricity.

Dias et al.[419] examined the possibility of increasing ethanol production from sugarcane through the hydrolysis of some of the bagasse to produce additional reducing sugars. The process is based on the well-established Organosolv process. The entire pathway was simulated to understand the trade-offs between diverting bagasse from power generation (combustion) to production of ethanol and coproducts. The simulation was based on a large-scale sugar facility (1000 m^3/day ethanol production) where the bagasse is processed via three-stage hydrolysis.

Stage 1 involves pretreating the bagasse (50 wt % moisture content) with dilute sulfuric acid at ~122 °C and 200 kPa, which removes hemicellulose from the bagasse producing a pentose liquor.[419] Conversion of hemicellulose to pentose of ~80% can be achieved. There are no known pathways for converting pentose into ethanol, although it can be converted into other products such as butanol or xylitol. The solid residue from stage 1 contains cellulose and lignin. In stage 2, the lignin is dissolved using 40−60 wt % ethanol with sulfuric acid as catalyst via the Organosolv process. In stage 3, the cellulose is recovered as a solid and hydrolyzed using sulfuric acid at ~200 °C and 36 bar pressure and conversions of ~80% of the cellulose into hexose can be achieved. Finally the hexose liquor can be mixed with the sugarcane juice and fermented to ethanol.[419]

It was determined that the key to optimization of this process was the configuration of the distillation columns.[419] When conventional (single pressure) distillation is used, ~75% of the bagasse can be diverted from power generation to hydrolysis. On this basis, 102.5 L of anhydrous ethanol can be produced per ton of sugarcane with 33.0 kWh/ton electricity available for sale. This is an increase of 22.5% ethanol relative to conventional ethanol production. If double-effect distillation columns are used then 90 wt % of the bagasse can be used for hydrolysis. In this case, 105.7 L of anhydrous ethanol could be produced per ton of sugarcane (a 26.3% increase compared to conventional) and 13.5 kWh/ton electricity. In both these cases, it was assumed that cane trash and lignin are used as fuels for power and steam generation at the plant. Additional revenue could be obtained from the pentose liquor, as the values above were derived solely from the conversion of hexose to ethanol.

Kong et al.[420] investigated butanol production from sugarcane bagasse via hydrolysis in the presence of gamma-valeroacetone (GVA) using the ABE method (acetone-butanol-ethanol). Hydrolysis of the bagasse after delignification in a GVA-water solution gave a relatively high reducing sugars yield of 840 mg/g feedstock.

Robl et al.[421] studied the use of enzyme mixtures for the production of reducing sugars from hemicellulose and cellulose in sugarcane bagasse. A hydrothermal pretreatment was used prior to hydrolysis. The use of multiple enzymes from ascomycete strains increased the fermentable sugar yields by 120 to 238% compared to conventional practices.

Sakdaronnarong et al.[422] examined the use of various heterogeneous catalysts and solvents in a aqueous biphasic system for the hydrolysis of sugarcane bagasse. A maximum reducing sugars yield of ~97% was achieved using a carbon-based catalyst; however, the authors concluded that the use of a magnetic metal-based catalyst was more feasible for commercial scale operations due to ease of catalyst recovery.

Namchot et al.[407] explored the use of solid carbon-acid catalysts for the hydrolysis of sugarcane bagasse. Solid carbon-acid catalysts were first produced from cellulose, lignin, and bagasse via carbonization using dry-pyrolysis or HTL followed by sulfonation. A catalyst was also produced by direct sulfonation of the lignin (without carbonization). The activity of all the catalysts was compared to commercial acid catalysts (Amberlyst 15 and phosphotungstic acid). The catalysts were used to hydrolyze delignified bagasse, cellulose, and starch. In summary, the solid-acid catalysts from lignin and sugarcane bagasse were the most effective. Yields of total reducing sugars from bagasse, cellulose, and starch when using the sugarcane bagasse derived catalyst were 18%, 28%, and 88%, respectively; yields from the lignin catalyst were 65%, 46%, and 97%, respectively. An important finding was that the solid-acid catalyst produced by direct sulfonation of lignin showed equal or higher activity than the one produced from carbonized lignin. For a useful overview of studies on the various types of catalysts being developed and carbonaceous-acid catalysts, refer to the original publication (ref 407) and citations therein.

Braga et al.[423] studied fungal strains for their ability to produce accessory enzymes to improve reducing sugars yield from hydrolysis of pretreated sugarcane bagasse. An improvement of ~36% sugar yield was observed when xylanase and feruloyl esterase (accessory enzymes) were used in conjunction with a commercial enzyme.

Kaar et al.[424] studied the effectiveness of steam explosion of sugarcane bagasse followed by enzymatic saccharification to produce monosaccharides. Treatments spanned a range of reaction temperatures and reaction times, and the resulting material samples were evaluated for their ethanol potential, based on complete conversion of the cellulose and hemicellulose fractions of the feedstock. Ethanol potential values, ranging from 36 to 64%, were limited by trade-offs between glucose and xylose yields across the range of reaction conditions.

Eucalyptus: Vargas et al.[410] used a process optimization model to compare one- and two-step pretreatment methods used to improve accessibility to cellulose for the production of fermentable sugars via enzymatic hydrolysis of *Eucalyptus globulus*. The results suggest there is little difference between using a one-step dilute acid pretreatment on the amount of fermentable sugars obtained compared to a two-step method using steam explosion or autohydrolysis followed by a posthydrolysis step. Autohydrolysis refers to a hot water pretreatment which dates back to the 1940s.[425]

Costa et al.[426] studied the use of acid sulfite pretreatment on the enzymatic hydrolysis of *Eucalyptus globulus*, *Pinus pinaster*, and *Cytisus stratus*. It was found that the effectiveness of the pretreatment was highly species dependent. Relatively mild conditions were required for eucalyptus which released mainly xylose and achieved ~80% polysaccharide conversion during enzymatic hydrolysis. In comparison, pine conversion was ~13%.

Carvalho et al.[412] investigated the optimal conditions for cold alkaline extraction as a pretreatment for the semi-simultaneous saccharification and fermentation of eucalyptus, sugarcane bagasse, and sugarcane straw (trash) for ethanol production. The success of the approach at improving ethanol yields is due to the effective removal of hemicellulose and lignin which improves access to the cellulose. Similar glucose yields were obtained from all three feedstocks; however, the greatest yield of ethanol (65 mg ethanol/g biomass), concentration (5.74 g/L), and productivity (0.57 g/L per h) were obtained from the sugarcane straw.

Messaoudi et al.[427] examined the use of an "instant controlled pressure drop" (DIC) pretreatment to improve the enzymatic hydrolysis of eucalyptus chips in relation to ethanol production. The maximum yield of reducing sugars obtained using the DIC pretreatment was ~85 g reducing sugars/100 g dry feedstock compared to ~70 g after dilute-acid pretreatment and ~25 g for the untreated eucalyptus.

Castro et al.[428] investigated a dilute phosphoric acid impregnation steam explosion pretreatment to enhance ethanol production from enzymatic hydrolysis of *Eucalyptus benthamii*. The fermentation of hemicellulose and cellulose derived sugars was also studied. Using optimized conditions ethanol yields of 240 g ethanol/kg biomass were obtained which are among the highest yields reported for a eucalyptus feedstock.

Huo et al.[429] used a combined alkali impregnation and refining (pulping) pretreatment to enhance reducing sugar yields via the enzymatic hydrolysis of eucalyptus chips (species not stated). The maximum yield of reducing sugars was ~91% of the theoretical yield.

Kobayashi et al.[430] developed a reusable heterogeneous catalyst for the hydrolysis of eucalyptus (species was not stated). A carbon-based catalyst was also produced from eucalyptus by air oxidation. When hydrolysis was performed in water with no catalyst, the yields of glucose and xylose were 3 and 30%, respectively; when the catalyst was used yields were 31 and 83%. Yields were significantly improved by using dilute HCl acid as solvent. HCl solvent without catalyst produced glucose and xylose yields of 32 and 26%, respectively, whereas the addition of catalyst increased yields to 78 and 94%, respectively, in the first hydrolysis cycle and 82 and 89%, respectively, in the second cycle (using recycled catalyst).

Leucaena: Only two studies on the recovery of fermentable sugars from leucaena wood were identified (*Leucaena diversifolia*). The research was aimed at the recovery of hemicellulose sugars and delignification of the wood to produce cellulose in a form that could be used for pulp paper processing.[431,432] The process involved a HTL pretreatment (autohydrolysis) to remove hemicellulose and delignification via an ethanol-sodium hydroxide-anthraquinone process. Around 50 wt % of the hemicellulose was removed from the wood chips as xylose, xylose polymers, and furfural.

Rice Straw: Goswami et al.[408] used a solid carbon-acid catalyst to improve the yield of reducing sugars from the hydrolysis of rice straw. Raw rice straw and alkali pretreated rice straw were studied. The carbon-acid catalyst produced reducing sugars yields of 147 mg/g of raw rice straw and 262 mg/g of alkali pretreated rice straw. The main advantage from the use of a solid catalyst is the ease of recovery and recyclability. Refer to the original publication (ref 408) and citations therein for further details of solid carbon-acid catalyst.

Dayanandan et al.[433] used a fungus and its enzymes to produce fermentable sugars from alkali pretreated rice straw. Hydrolysis yielded a reducing sugars concentration of 33.6 g/L. Srivastava et al.[434] achieved improved yields of reducing sugars from alkali pretreated rice straw using crude cellulase activated with nanocomposite Fe_3O_4/alginate compared to a control.

Rawart et al.[435] studied the cellulolytic enzyme production potential of three types of *Aspergillus spp*. for use in the hydrolysis of rice straw. Of the strains tested, *Aspergillus niger* produced the highest concentration of cellulase. The concentration of reducing sugars from the hydrolysis of rice straw using the crude cellulase from *A. niger* was 66.2 g/L with a productivity of 2.75 g/L per hour.

Li et al.[436] optimized the sulfur trioxide microthermal explosion pretreatment conditions for the production of reducing sugars from rice straw via enzymatic hydrolysis. The process was effective at removing the hemicellulose and lignin from the rice straw; the main components in the hydrolysate were glucose and xylose.

Yang et al.[437] examined the enzymatic hydrolysis of rice straw using a tubular reactor coupled to a ultrafiltration membrane for the production of reducing sugars. The process was successful in producing high yields of reducing sugars through the effective removal of inhibitory products.

Suwannatangsee et al.[438] studied the production of enzymes for the hydrolysis of rice straw, looking at synergies between using fungal enzyme extracts in combination with commercial cellulase. A maximum yield of 769 mg of reducing sugars/g biomass was achieved under optimized conditions.

Lin et al.[439] reported results from a pilot-scale ethanol production plant using rice straw feedstock where *Pichia stipitis* was used to ferment the sugars from hemicellulose. The maximum ethanol yield was 440 mg per g of reducing sugars in the hydrolysate. For comparison, the theoretical maximum yield of ethanol from reducing sugars using yeast fermentation is 510 mg/g.

Huran et al.[440] compared the effectiveness of two "ammonia fiber expansion" (AFEX) pretreatments as a function of biomass particle size using rice straw for the production of reducing sugars. The maximum reducing sugars yield was 486 mg/g pretreated rice straw (~76% of the theoretical maximum).

Rice Husks: Sharma[441] reported a two-step process for converting sugarcane bagasse and rice husks into fermentable sugars for the production of ethanol using acid hydrolysis in

1989. Ethanol was produced from glucose recovered from the cellulose fraction of the biomass and furfural was produced from hemicellulose derived xylose. It was also suggested that the lignin could be hydrocracked to produce phenol and hydrocarbons.

Megawati et al.[442] assessed the role of the sulfuric acid catalyst concentration on the kinetics of fermentable sugars production from the hydrolysis of rice husks. Nikzad et al.[443] compared three pretreatment methods for the production of reducing sugars from the hydrolysis of rice husks. The methods included dilute sulfuric acid (1% v/v, 121 °C, 30 min), dilute sodium hydroxide (3% v/v, 121 °C, 30 min), and heat treatment (121 °C, 30 min). The greatest yields of reducing sugars was obtained using the dilute NaOH pretreatment.

Rabah et al.[444] examined the hydrolysis of rice husks and ground nut shells using various concentrations of dilute HCl and compared the ethanol yield when using *S. cerevisiae* and *Z. mobiliz*. The main findings were that roughly the same yields of reducing sugars were achieved from both feedstocks under optimized conditions. The ethanol yields were largely independent of the enzyme used; however, when the two enzymes were used in conjunction, the ethanol yield was significantly lower.

Khoo[411] reviewed 55 lignocellulose to ethanol pathways and pretreatments for sugarcane bagasse, rice straw and husks, switchgrass, and corn stover. A sustainability assessment was also performed based on land footprint projections, using the production of 1 million L of ethanol to compare the feedstocks. Sugar cane bagasse and rice straw were deemed to be the most productive, requiring land footprints of 80−85 ha-year. Switchgrass and corn stover were the least productive requiring 140 and 366 ha-year, respectively.

Banagrass: No studies on fermentable sugar production from banagrass were identified, although there are a large number of publications for Napier grass and a few on elephant grass. It should be noted that many of the studies have no relevance to jet fuel production.

Turn et al.[445] studied steam explosion of banagrass in a 10 L reactor system. Gas phase carbon loss from the explosion process, the focus of the study, equaled ~0.5−2.4% of feedstock carbon and increased with increasing severity.

Pensri et al.[446] studied the potential for reducing sugars production from Napier grass residue used for biogas production. A sodium hydroxide pretreatment was used prior to enzymatic hydrolysis. Under optimized conditions, a fermentable sugars yield of 770 mg/g of pretreated residue (64 g/L) with a glucose yield of 522 mg/g (43 g/L).

Bensah et al.[447] investigated the ethanol production potential for five types of west African biomass (elephant grass, bamboo wood, rubber wood, Siam weed, and coconut husks) using wheat straw as a control. The effectiveness of a hydrothermal pretreatment (195 °C, 10 min) prior to enzymatic hydrolysis was examined as a way to increase fermentable sugars yields. When the hydrothermal pretreatment was used, sugar yields were 3.5 times greater than for the untreated sample. Of the African samples, elephant grass produced the greatest yields of glucose and ethanol (16.1 g/100 g total solids (TS)) which was similar to that obtained from wheat straw (15.3 g/100 g TS).

Wen et al.[448] used a biological (microbial) pretreatment followed by a concurrent enzymatic hydrolysis and anaerobic digestion process to produce reducing sugars and biogas from Napier grass. Significant variations in fermentable sugar yields were observed for the three microbial consortia tested, ranging from ~44% to 83% of the theoretical yield. When the microbial pretreatment was used, methane yields were also increased by a factor of 1.3−1.5 compared to an untreated control sample.

Menegol et al.[409] investigated the use of surfactants to increase the yield of reducing sugars from the enzymatic hydrolysis of elephant grass. This is based on addressing the problem of loss of cellulase activity due to its irreversible absorption onto cellulose surfaces through the use of surfactants. It was demonstrated that improved yields of reducing sugars could be obtained in the presence of the surfactants tested. It was also shown that larger biomass particles could be used than for the conventional process while maintaining sugar yields, hence less energy is required for particle size reduction when a surfactant is used.

Yang et al.[449] produced bacterial (microbial) cellulose from elephant grass using acid hydrolysis and *Gluconacetobacter xylinus*. The aim is to produce a high-value cellulose material for use in food, medical, and papermaking applications.

Energycane: No publications were identified for the production of fermentable sugars from fiber-energycane. One study has been published on ethanol yields from different varieties of sugar-energycane where reducing sugars were recovered from the juice and bagasse via dilute acid pretreatment and enzymatic hydrolysis.[450]

Sorghum: There are few publications on the hydrolysis of sorghum and, with one exception, all were for sweet or grain sorghum, crops not targeted for this review. Varquez et al.[451] tested the use of phosphoric acid to hydrolyze *Sorghum bicolor* straw (Mexico) for the production of furfural from the pentose fraction of the hydrolysate. A maximum yield of 134 mg of furfural per dry g sorghum straw was achieved, which is comparable to yields obtained from other types of biomass that are used for the commercial production of furfural.

Sesbania: Two publications related to the production of sugars from the hydrolysis of sesbania were identified. Yanez et al.[452] examined the effectiveness of autohydrolysis pretreatment for the production of xylooligosaccharides from *Sesbania grandiflora*. Using optimized conditions, 63% conversion was achieved. Baskar et al.[453] tested a nanobiocatalyst (cellulase bound magnetic nanoparticles) for the hydrolysis of *Sesbania aculeate* in relation to ethanol production. The main focus of the paper was on the characterization of the catalyst; nonetheless the authors stated that the process was an efficient way of producing ethanol and that the catalyst was reusable.

Glyricidia: No publications were identified.

3.2.5. Alcohol Production.

It should be noted that the previous section (Section 3.2.4.1 Sugars Production) describes hydrolysis processes for the production of sugars but *not* their conversion to alcohols or other products. This section discussed the conversion of sugars (from any source, not just from hydrolysis) to alcohols.

The alcohol to jet fuel process (ATJ) relies on a ready supply of alcohols as feedstock. Alcohols can be produced from sugar and starch crops or lignocellulosic biomass, including manure, sewage sludge, and MSW, via numerous thermo- and biochemical process routes. Figure 24 provides an overview of some process routes being studied for alcohols production.[454]

Fuel ethanol production from corn starch or sugarcane (first generation feedstocks) are well established processes that have been operated at commercial scale for over 30 years.[406] Menetrez[455] has reviewed ethanol production facilities using

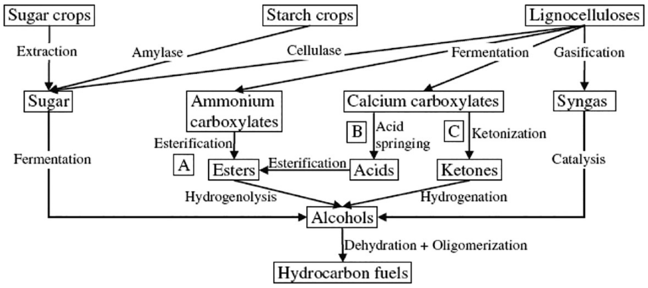

Figure 24. Overview of pathways being considered for producing alcohols from various feedstocks for use in alcohol to jet processes. Reprinted by permission from Springer Nature, *Journal of Industrial Microbiology and Biotechnology*, Techno-economic analysis of biomass to fuel conversion via the MixAlco process, Pham, V.; Holtzapple, M.; El-Halwagi, M., Copyright 2010 (ref 454).

first generation and second generation (lignocellulosic) feedstocks as of 2014. There are few second generation plants currently operating and most are demonstration scale facilities.

Some of the process routes for alcohols production are discussed below; this is in no way an exhaustive review of the subject. For further details on fermentation-based processes, readers are referred to publications by Holtzapple[363,454,456−458] and Dumesic (who has also examined thermochemical routes and water phase processes and combinations of these approaches).[387,414,459,460] Kumar and Gayen[461] reviewed butanol production methods. For ethanol production via first and second generation feedstocks, also see Cui et al.[262] and Mentetrez.[455] Laluce et al.[462] reviewed progress in second generation ethanol production, focusing on methods for processing hemicellulose. Mosier et al.[363] reviewed pretreatment methods for ethanol production from second generation feedstocks.

A report published by SINTEF[231] reviewed the ATJ process in 2012 and concluded that the main barrier to the implementation of the process is the cost-effective production of the alcohol feedstock. There are a number of alcohols and long chain fatty alcohols that can be converted to jet fuel. Wang and Tao[223] have presented flow diagrams for conversion of methanol, ethanol, and iso-butanol to jet fuel. All the steps required for these conversions are mature technologies widely used in existing refinery operations, Figure 25 shows the main generic steps.[231] Nonetheless, there are continued research efforts to develop more efficient catalysts for the production of alcohols and their conversion to jet fuel, see Wang and Tao[223] and Guell et al.[231] for useful reviews of recent activities.

3.2.5.1. Costs, Mass, and Energy Balance for Alcohols Production. Pham et al.[454] reported a techno-economic analysis (TEA) in 2010 for the production of liquid hydrocarbon fuels (gasoline to diesel) via the MixAlco process. This is a fermentation based process that converts carbohydrates, proteins, and fats in biomass to carboxylate salts using acid-forming microorganisms. At a scale of 40 dry Mg feed input per hour, the minimum selling price (MSP) for liquid hydrocarbon fuels is U.S. $2.56/gallon (U.S. $1.75/gallon ethanol). This was derived by assuming a feedstock cost of U.S. $60/Mg, 10% return on investment and internal hydrogen production. The total capital investment is U.S. $5.54/annual gal of hydrocarbons (U.S. $3.79/annual gallon ethanol). Assuming a scale of 400 Mg/h feed input reduces the MSP to U.S. $1.76/gallon hydrocarbons (U.S. $1.20/gallon ethanol), the authors report this price is competitive with petroleum derived fuels when the cost of a barrel of crude oil is ∼ U.S. $65. Production costs are greatly reduced if the feedstock is municipal solid waste. A tipping fee of $45/Mg and a scale of 40 Mg/h yielded an MSP for hydrocarbons of $1.24/gallon (U.S. $0.85/gallon ethanol).

Humbird et al.[463] reported a detailed design case and economic assessment for ethanol production via dilute-acid pretreatment and enzymatic hydrolysis of corn stover. The theoretical yield of ethanol was 0.26 kg per kg dry biomass with a MSP of $2.15/gallon ($2007) for a plant with a scale of 2 205 dry ton/day biomass input. Carbon conversion from the feed to ethanol was 29%. The major carbon losses are due to combustion of the lignin byproduct. The energy efficiency for conversion of biomass to jet fuel via ethanol is 29% based on the energy content of the feedstock relative to that in the jet fuel product.[231]

NREL and partners[261] published a TEA in 2012 that examined the costs of mixed alcohols production via gasification-FT. It was concluded that steam blown gasification at low pressure (33 psi) using an indirectly heated dual-bed design (circulating entrained flow design) is more cost-effective than other gasification technologies.[261] However, it should be noted that circulating dual bed reactors are more complex to operate than traditional fluidized bed designs, and there is limited information on operating or maintenance costs due to limited experience at the commercial scale (particularly for extended periods of operation).

Mass Balance from NREL 2012 Report[261]: Product yields in terms of gallons of ethanol per dry U.S. ton were 83.8 gallon of ethanol and 10.1 gallon of higher alcohols (350 and 43 L, respectively).[261] At a scale of 2 000 Mg per day dry biomass input (wood, 0.93 wt % ash), the yield of ethanol was ∼65 million gallons per year and ∼8 million gallons per year of higher alcohols.

Energy Balance from NREL 2012 Report[261]: The energy content of the product alcohols accounted for ∼45% of the total energy input to the plant in terms of dry wood on a lower heating value basis, with 40% in the form of ethanol and 5% as higher alcohols.[261] It should be noted that in the cited analysis there were no external energy inputs to the plant; all electricity and other energy inputs were produced by combusting part of the producer gas. The main energy loses were due to air cooled heat exchangers (23%) and electrical and thermal losses (11%); energy losses due to moisture and other water inputs accounted for 15%.

Costs from NREL 2012 Report[261]: A minimum ethanol selling price (MESP) of $2.05/gallon was reported with the main contributions coming from feedstock ($0.735) and producer gas compression and expansion ($0.667), followed by the gasifier ($0.277).[261] The price of the feedstock used in the cited study was $61.57 per dry U.S. ton delivered to the plant.

Figure 25. Main steps of the ATJ process.

Table 41. Summary of Mass and Energy Balances for AJF Production[a]

parameter		process				
		L-Eth	SYN-FER	GFT	HEFA	S-Eth
feed	lignocellulosic (dry Mg/h)	77.88	77.88	77.88		
	vegetable oil (Mg/h)				14.78	
	sugarcane (dry Mg/h)					63.27
	cane trash (dry Mg/h)[b]					31.16[b]
product	jet fuel (Mg/h)	7.75	7.94	7.93	7.14	7.76
	naphtha (Mg/h)			2.39	1.71	
	diesel (Mg/h)	1.01	1.04		0.31	1.01
	electricity (MW)	19.1		12.5		52.6
specific hydrogen usage (kg-H_2/Mg-fuel)		12.1	12.1	23.2	65.3	12.1
jet fuel to feed energy ratio		25.3%	26.2%	26.1%	58.6%	22.6%
overall energy efficiency		33.3%	29.6%	37.2%	75.3%	37.1%

[a] Reprinted from *Bioresource Technology*, Vol. 216, Diederichs, G. W.; Ali Mandegari, M.; Farzad, S.; Görgens, J. F., Techno-economic comparison of biojet fuel production from lignocellulose, vegetable oil and sugarcane juice. pp 331−339, Copyright 2016, with permission from Elsevier (ref 465); refer to the original publication for a more extensive breakdown of mass and energy balances. [b] The cane trash is combusted to produce steam and electricity.

Another process route that has been studied in detail is methanol-to-gasoline (MTG) via biomass gasification. Phillips et al.[464] reported a design case and TEA for conversion of poplar wood chips (50 wt % moisture) at a scale of 700 000 tons/year input. The mass balance in terms of gasoline was ∼230 L/ton dry feedstock with ∼39 L/ton of LPG as coproduct. Energy efficiency was ∼37.7% for gasoline alone and 42.6% when coproducts were included, significantly more efficient than a fermentation process using corn stover (assuming a plant of similar scale).

A report from SINTEF[231] compared the costs of the four TEAs outlined above after normalizing the plant scale to 289 MW_{th} input. The gasification routes have lower equipment costs; U.S. $120 million for mixed alcohols and U.S. $110 million for the MTG process. The two fermentation processes have costs of U.S. $230 million and U.S. $170 million. It is difficult to directly compare the efficiencies and production costs of these processes as feedstocks, process assumptions, and the final products were different (i.e., liquid hydrocarbons, ethanol, gasoline).

Atsonios et al.[251] reported a detailed review of process routes and costs for jet fuel production via conversion of biomass to alcohols using thermochemical and biochemical methods. A comparison of three gasification based routes was also provided: (1) gasification to ethanol to jet fuel, (2) gasification to butanol to jet fuel, and (3) gasification-FT to jet fuel. In all cases an oxygen-blown pressurized circulating fluidized bed gasifier was selected. These process routes could produce ∼0.14 to 0.17 kg jet fuel per kg feedstock, which is greater than the biochemical pathways. Roughly one-third of the carbon in the feedstock is converted to jet fuel with a thermal efficiency of ∼40% via the gasification routes (based on LHV of wood input and LHV of jet fuel produced). Approximately 20% of the carbon in the feedstock is lost as CO_2 during gasification, an additional 20% during the water gas shift of CO to H_2, and another 30% during jet fuel synthesis and finishing. The alcohol route requires greater power consumption than the FT route; however, FT produces less jet fuel with lower carbon conversion. A thermochemical plant operating at 190 MW_{th} input had an associated water consumption of ∼640 000 m^3/year.

Wood feedstock at a cost of €60/dry Mg (€2011) and a conversion facility sized for 190 MW_{th} input (846 dry Mg/day) were used to calculate MSPs of €1.24/L jet fuel and €1.49−1.28/L from the FT and alcohol routes, respectively.[251] The latter range of MSPs depended on the catalyst used. Total capital cost for the FT plant was ∼€207 million and €242−248 million for the alcohol routes. The lowest production costs were from fermentation routes, €0.83/L jet fuel (corn stover €49/dry t or wheat straw €18/dry t), at a scale of 2000 dry Mg/day input. At this scale the gasification alcohol route cost was ∼€1.02/L jet fuel. It should be noted that the cost analysis for the biochemical routes was less rigorous than for the thermochemical pathways. On a normalized scale, the biochemical routes have significantly lower capital costs but almost double the operating costs of the thermochemical pathways. An important finding was that the cost estimates for fuel products via ATJ-like process routes have increased over the years as more accurate data becomes available, ranging from ∼€10−15/GJ (HHV) in 1999 to €22−40/GJ in 2015.[251]

Wang and Tao[223] published a useful review of the main process routes used for production of jet fuel from biomass, covering technical, economic, and environmental aspects. Butanol produced from the acetone-butanol-ethanol (ABE) fermentation route from a sugar crop (corn, US $79.23/ton) had a MSP of US $1.04/gal (US $0.34/kg). The price increased to US $3.7/gal (US $4.1 GGE) when cellulosic biomass was used as feedstock (2011 $).

Diederichs et al.,[465] reported a techno-economic comparison of five processes for jet fuel production from first and second generation biomass. First generation refers to vegetable oils and sugarcane juice and second generation to lignocellulosic biomass. The first generation feedstocks were processed via (1) hydroprocessing of vegetable oils (HEFA) , (2) sugarcane juice to ethanol via fermentation and upgrading (S-Eth). The second generation feedstocks were processed using (3) gasification-FT (GFT), (4) biochemical conversion to ethanol with upgrading (L-Eth), and (5) gasification where the producer/synthesis gas is fermented to ethanol followed by upgrading (SYN-FER).

The GFT route was based on a process defined by Petersen et al. in 2015[290] assuming steam and oxygen blown gasification in a dual fluidized bed reactor operating at ∼900 °C and atmospheric pressure. Approximately 42 wt % of the biomass was combusted to generate steam and electricity to power the process. The same basic gasification configuration was assumed

Table 42. Summary of Costs for AJF Production[a]

parameter		L-Eth	SYN-FER	GFT	HEFA	S-Eth
variable operating cost (million U.S.$ per year)	raw materials and waste disposal	120.23	69.75	62.51	112.60	85.36
	byproducts credits	24.77	13.03	38.16	25.44	38.28
fixed operating costs. (million U.S.$ per year)		24.78	22.09	27.85	10.52	18.92
TIC (million U.S.$)		274.2	232.8	321.3	91.7	184.1
FCI (million U.S.$)		482.6	409.7	565.5	161.4	324
FCI (annual jet fuel, $/kg)		7.90	6.54	9.05	2.87	5.30
TCI (million US$)		532.7	452.5	623.9	179.4	358.3
MJSP ($ per kg jet fuel)		3.43	2.49	2.44	2.22	2.54

[a] Reprinted from *Bioresource Technology*, Vol. 216, Diederichs, G. W.; Ali Mandegari, M.; Farzad, S.; Görgens, J. F., Techno-economic comparison of biojet fuel production from lignocellulose, vegetable oil and sugarcane juice. pp 331−339, Copyright 2016, with permission from Elsevier (ref 465). TIC, total investment cost; FCI, fixed capital investment; TCI, total capital investment; MJSP, minimum jet fuel selling price.

for both gasification pathways, see the original publication (ref 465) for details on the assumptions used, process flow diagrams, and mass and energy balances. The L-Eth process is based on hydrolysis and fermentation of lignocellulosic biomass as reported by Petersen et al.[466] and Humbird et al.[463] The S-Eth process converts fermentable sugars to ethanol followed by upgrading to jet fuel. The HEFA process is based on the hydroprocessing of vegetable oils followed by cracking and isomerization to jet fuel range hydrocarbons.[465] The lignocelluosic feedstock was assumed to cost 96.6 $/dry Mg (2014 $), sugarcane 41.0 $/wet Mg and vegetable oil 956.3 $/Mg.[465] The mass and energy balances for the five processes are summarized in Table 41 and costs in Table 42.

In summary of the study by Diederichs et al.,[465] the minimum jet fuel selling prices (MJSP) for jet fuel produced by the five processes examined are significantly greater than conventional jet fuel (2−4 times higher). The lowest MJSP was for HEFA (2.22 $/kg jet fuel) followed by the gasification processes (2.44−2.49 $/kg), with the routes via ethanol having the greatest MJSP (Table 42). The main contributors to the costs were feedstock and fixed capital (and enzymes for the fermentation routes).

An observation from Wang and Tao[223] is that there is insufficient information available to make a detailed comparison of ATJ process routes or for the production of alcohols in general. This includes a lack of mass and energy balances as well as production, capital, and operating costs. One life cycle analysis for ATJ processes was identified, where a 60−75% reduction of greenhouse gas emissions was estimated relative to fossil derived jet fuel; this compares to an 85−105% reduction for FT processes and 77−80% for HTL.[467] In addition, there is a need for studies on lower cost feedstocks such as agricultural residues and organic waste (manure, sludge, MSW, etc.) as well as algae and tropical biomass species. A review of data for tropical species is presented below in section 3.2.5.2.

A number of companies are working toward commercialization of ATJ processes.[223,231,251] Briefly, GEVO (USA) produces renewable isobutanol via fermentation of sugar crops and cellulosic biomass. LanzaTech (New Zealand) produces fuels and chemicals via fermentation of gases from gasification and waste gases from industrial processes (steel production, etc.). Swedish Biofuels (Sweden) produces gasoline, diesel, and jet fuel from alcohols produced via fermentation. Zeachem (USA) is producing ethanol and fuels by a combination of gasification and fermentation. Ineos Bio (USA) is producing ethanol via fermentation of producer gas from gasification of organic materials.

Summary of Mass and Energy Balances (ATJ): A summary of product yields for jet fuel produced by various ATJ processes, intermediates, and feedstocks have been reported[223] as well as breakdowns of individual intermediate yields as a function of process conditions (temperature, pressure, catalyst, process route) for selected pathways. In summary, yields range from ~7 gallons of jet fuel/dry Mg biomass for unrefined sugar (where unrefined sugar is the feedstock/biomass) to ~70 gallon/dry Mg for corn stover, wheat straw, barley straw, and whey permeate. Energy balances depend on the process details, which are largely unknown.

Based on the studies discussed earlier in this section, the yield of ethanol is 0.26 kg/dry ton corn stover when using dilute-acid pretreatment and enzymatic hydrolysis.[463] Carbon conversion and energy efficiency were 29%. From NREL's 2012 publication,[261] the ethanol yield is 83.8 gallon/ton dry wood plus an additional 10.1 gallon higher alcohols when using gasification-FT. Energy efficiency is ~45% on LHV basis for total alcohols. Phillips et al.[464] reported a gasoline yield of 230 L/ton dry popular woodchips and 39 L LPG/ton from gasification using the MTG approach. Energy efficiency is ~43% when considering coproducts. Atsonios et al.[251] reported mass balances of 0.14−0.17 kg jet fuel/kg dry wood for three gasification pathways via ethanol, butanol, or direct FT to produce jet fuel. Energy efficiency of ~40% was derived for the three routes on a LHV basis.

A study by Diederichs et al.[465] reported a mass balance of ~25% for jet fuel production from lignocellulosic biomass to ethanol via hydrolysis. This is roughly the same as gasification routes using either fermentation of the producer gas or FT to produce ethanol (~26%). In terms of energy efficiency, the gasification FT route was the highest (37%), followed by hydrolysis (33%), and fermentation of producer gas the lowest (30%).

Summary of Costs: Accurate information on capital and production costs are not available for a complete ATJ process;[223] however, cost analyses are available for the production of the alcohol intermediates.[223] These include ethanol at 2.5−2.6 U.S. $/gallon (3.8−4.0 $/GGE), *n*-butanol at 3.7 $/gallon (4.1 $/GGE), iso-butanol at 3.6 $/gallon (4.0 $/GGE), and methanol at 1.5 $/gallon (3.0 $/GGE).

Based on the studies discussed earlier in this section, the MSP of liquid hydrocarbons via the MixAlco approach is 2.56 $/gallon hydrocarbon at a scale of 40 Mg per h or 1.76 $/gallon at 400 Mg per h.[454] For ethanol produced from corn

Table 43. Summary of the Strengths and Weaknesses of Alcohol to Jet Process Routes[a]

strengths	weaknesses
• The main steps to convert alcohols to jet fuel are mature commercial scale technologies.	• Alcohol production costs are high, especially for lignocellulosic biomass.
	• limited experience with alcohols other than methanol/ethanol
• feedstock flexible, sugar crops, starch crops, lignocellulosic biomass and MSW.	• Process routes are not optimized.
• The jet fuel produced contains aromatics, meaning it is not necessary to blend with petroleum derived fuels.	• inherent challenges to working with living microorganisms
• relatively small hydrogen requirement (~1 kg/800 kg dry biomass input)	• Production rates when working with living microorganisms are low by chemical refinery standards.
• For fermentation routes, the alcohol to hydrocarbon reactions are highly selective producing high yields of the desired product.	• Microorganisms are sensitive to impurities that inhibit their activity, including their own byproducts.
	• high enzyme cost

[a] Reprinted from *Renewable and Sustainable Energy Reviews*, Vol. 53, Wang, W.-C.; Tao, L., Bio-jet fuel conversion technologies, pp 801−822, Copyright 2016, with permission from Elsevier (223). Reproduced with permission from Guell, B. M., Bugge, M., Kempegowda, R. S., George, A., Papp, S. M. Benchmark of conversion and production technologies for synthetic biofuels for aviation (ref 231). Copyright 2012 SINTEF Energy Research.

stover using dilute-acid pretreatment and enzymatic hydrolysis, the MSP is 2.15 \$/gallon at a scale of 2200 dry tons per day. NREL's study calculated a 2.05 \$/gallon MSP for ethanol produced at a scale of 2000 dry Mg wood per day using gasification-FT. Atsonios et al.[251] reported a MSP of 1.24 \$/L (\$4.69/gallon) jet fuel from wood gasification-FT and 1.28−1.49 \$/L jet fuel for ethanol or butanol production via gasification followed by conversion to jet fuel at a scale of 846 dry Mg/day input. The MSP from the biomass hydrolysis route is 3.43 \$/kg jet fuel, 2.49 \$/kg jet fuel via fermentation of producer gas from gasification, and 2.44 \$/kg jet fuel via gasification FT.[465]

Strengths and Weaknesses of ATJ Processes: The strengths and weaknesses of the ATJ process and the production of alcohols from nonfood crops and other organic materials are outlined in Table 43.

3.2.5.2. Alcohols from Tropical Biomass Species. Enzymatic and acid hydrolysis are the most widely studied approaches to producing alcohols from biomass and are used widely at the commercial scale for first generation feedstocks (i.e., sugar and starch food crops such as sugarcane and corn). There are also a a great number of lab- to pilot-scale studies of second generation feedstock (lignocellulosic biomass and waste materials) including woody biomass, corncob, wheat straw, barley straw, winter rye, oilseed rape, fava bean, rice straw, and rice husks.[442] The complete process has not been demonstrated to be viable on a commercial scale (as of 2016)[223] as described in the previous section; this remains the case at the time of writing (March 2018).

Relatively few studies of tropical biomass species have been reported with the exception of sugarcane bagasse, rice husks, and rice straw. A number of thermo- and biochemical approaches (or in combination) are under investigation for the production of alcohols from second generation feedstocks. The fermentation of sugars into ethanol is *not* discussed in this section; refer to the sugars section for details of those methods (section 3.2.4).

Woody Biomass: No publications on alcohol production from eucalyptus or leucaena grown in tropical locations were identified other than those involving the use of hydrolysis and fermentation that were discussed in section 3.2.4. Due to a lack of information on tropical woody biomass, examples for methanol production from Japanese woods are provided.

Hasegawa et al.[468] compared the yields, energy efficiencies, carbon conversions, and CO_2 mitigation potentials of methanol production via FT-synthesis and ethanol from hydrolysis-fermentation. The wood feedstock was assumed to be from Japanese forest residues with a composition of 41.4 wt % cellulose, 28.1 wt % hemicellulose, and 30.5 wt % lignin (dry basis) with a LHV of 15.0 MJ/kg at 15 wt % moisture content (ash content was not reported). Methanol production was based on entrained flow gasification using steam and O_2 at a temperature of 800−1000 °C and a feedstock particle size of 1−2 mm. FT synthesis was conducted at 6−8 MPa and 200−300 °C with Cu/ZnO based catalysts. Ethanol production was based on acid hydrolysis (concentrated sulfuric acid) and fermentation using a genetically modified fungus (KF7-7M), conventional distillation, and zeolite membranes for dehydration.

The conversion of wood (15 wt % moisture) to methanol was 510 L/ton (wet basis) or 290 L/ton for ethanol.[468] The methanol energy yield was 8.4 GJ/ton wood, and ethanol was slightly lower at 6.2 GJ/ton wood. Energy efficiencies for methanol and ethanol production were 39% and 42%, respectively. Note that methanol requires greater electricity consumption. Carbon conversion efficiencies were 40 and 30% for methanol and ethanol production, respectively, and differences in CO_2 mitigation were small. In the cited study, it was assumed that the alcohols would be used as direct replacements for gasoline, either through blending or to power a fuel cell or flexible fuel vehicle.

Kumabe et al.[469] performed an economic and environmental analysis of methanol production from biomass gasification. The analysis was based on steam gasification of Japanese cedar at a scale of 400 dry ton/day input; for further details of the assumptions used refer to the original publication (ref 469). Three cases were compared: (1) where heat and power were purchased externally (fossil based), (2) where additional wood is combusted to generate heat and power, and (3) where heat and power were cogenerated using a combustion boiler and steam turbine.

Case 1 produced the greatest yield of methanol (47.7%) but required external inputs of 2.65 MW of heat and 5 MW of electrical power.[469] Case 2 produced a methanol yield of 36.1% with no additional heat input required and reduced external electrical power of 3.7 MW. Case 3 produced the lowest yield of methanol (30.9%) with no external heat or electrical inputs. Capital and operating costs are summarized in Table 44, and a detailed breakdown of the costs are provided in the original publication.[469] Costs are based on conditions in Japan,

Table 44. Capital and Operating Costs for Methanol Production from Gasification of Japanese Cedar[a]

case no.	capital cost k¥/m^3 methanol	operating cost k¥/m^3 methanol
1	15.1	21.3
2	17.7	14.0
3	46.3	16.0

[a] Reprinted from *Fuel*, Vol. 87, Kumabe, K.; Fujimoto, S.; Yanagida, T.; Ogata, M.; Fukuda, T.; Yabe, A.; Minowa, T., Environmental and economic analysis of methanol production process via biomass gasification. pp 1422−1427, Copyright 2008, with permission from Elsevier (ref 469.

assuming a zero cost feedstock. The authors note that Japanese cedar is a high-value and high-quality biomass (low ash content) and is therefore unlikely to be used for methanol production on a commercial scale.

Sugarcane Bagasse: The production of alcohols from bagasse has been extensively examined using a number of thermochemical and biochemical methods. A brief overview of some of these studies is provided below (excluding hydrolysis); refer to citations within the articles mentioned for further information.

Petersen et al.[466] made a TEA of ethanol and electricity coproduction using bagasse from South Africa. Six pathways were compared ranging from combustion of bagasse to generate electricity to various methods for the coproduction of ethanol produced from hydrolysis and fermentation of bagasse and electricity. Their analysis indicated that ethanol coproduction with electricity was more energy efficient than electricity production alone. The pathway achieving the greatest energy efficiency (∼33%) included vacuum distillation and biomass integrated gasification with combined cycle (VD/BIGCC). The least efficient process (∼15.5%) was electricity production alone using combustion with high-pressure steam cycles. From an economic point of view, the highest rates of return were for the VD/BIGCC process, which ranges from ∼30 to 41% depending on the assumptions used.

A number of gasification-FT based processes for the production of methanol or ethanol from bagasse have been reported,[290,466] including a comparison of FT with hydrolysis/fermentation.[289] Salient points from these studies have been summarized in the gasification section, section 3.2.1.1 (economics) and section 3.2.1.3 (in relation to tropical biomass, bagasse).

Fu and Holtzapple[457] examined batch anaerobic fermentation (1 L) of bagasse and chicken manure (80:20) to produce ammonium carboxylates which can subsequently be converted to mixed alcohols or hydrocarbons. Acid productivity of up to 1.27 g/L per day (grams of acid per liter of total liquids in all reactors) was achieved (76% conversion), and the highest yield was 0.37 g total acids/g volatile solids. In a related study, Fu and Holtzapple[456] examined the conversion of the same feedstock to calcium carboxylates using anaerobic fermentation. The highest acid productivity was 0.79 g/L per day, and the highest yield was 0.18 g total acids/g volatile solids fed. Modeling indicated that >80% conversion could be achieved under optimized conditions; conversion refers to VS digested divided by VS fed.

Thanakoses et al.[470] studied the counter-current fermentation of sugarcane bagasse from a sugar facility in Raceland, LA, with chicken manure to carboxylic acids (80:20 ratio) using mesophilic microorganisms. A comparison was made between microorganisms from terrestrial and marine sources. Maximum acid productivity of 2.49 g/L per day and 1.38 g/L per day were achieved using terrestrial and marine inoculums, respectively. Total acids yields of ∼0.35 g/g volatile solids fed were achieved using both inoculums. Using a model of the process, it was estimated that 90% conversion of biomass to carboxylic acids could be achieved at a concentration of 23.4 g/L when using marine inoculum.

Playne[471] studied carboxylic acid production from bagasse using a continuous fermentation process. Total acids productivity was 4.9 g/L per day with a yield of 0.25 g total acids/g of bagasse fed.

Tavasoli et al.[472] studied the catalytic hydrothermal liquefaction of Iranian sugarcane bagasse using potassium-promoted Cu/$\gamma$$Al_2O_3$−MgO nanocatalysts. The experiments were performed using a batch microreactor (0.25 g bagasse) at near critical water conditions (360 °C, 18 MPa) in reducing (H_2) and alkali (K_2CO_3) environments in the presence of various catalysts. The main aim was to investigate the role of Cu and K loadings on product yields and composition. When the unpromoted Cu/$\gamma$$Al_2O_3$−MgO catalyst was used, the greatest yield of hydrogen was achieved (10 mmol/g bagasse). The addition of potassium increased liquid yields and lowered gas yields (in particular the amounts of CO_2, CO, and H_2 decreased with increasing K). Potassium was found to favor alcohol and ester formation, and the maximum amount of alcohol and esters produced was 83.3 mmol/g bagasse (methanol, ethanol, and isopropanol were the main products).

Rice Straw: Agbogbo and Holtzapple[473] used counter-current fermentation with marine mesophilic microorganisms to produce mixed carboxylic acids from rice straw and chicken manure (80:20). The greatest acids productivity was 1.69 g/L per day, and the maximum total acids yield was 0.29 g/g volatile solids fed. Modeling predicted that conversion yields of 80% are possible.

In a related study, Agbogbo and Holtzapple[474] used a train of fixed bed fermentors to convert rice straw and chicken manure (80:20) to carboxylic acids using marine mesophilic microorganisms. The highest yields of total acids was 0.56−0.67 g/volatile solids fed. It was determined that system performance as measured by total acid concentrations, conversions, and yields was greater for the fixed bed design than from counter-current fermentation.

Rice Husks, Banagrass, Energycane, Sorghum, Sesbania, and Glyricidia (Gliricidia): No publications were identified, other than hydrolysis based approaches for producing reducing sugars followed by fermentation to alcohol.

4. CONCLUSION

Based on this review, croton, kamani, jatropha, and pongamia are promising candidates as oil producing crops. Banagrass, sorghum, sugarcane (bagasse), rice (husks and straw), and trees (eucalyptus, hybrid leucaena, gliricidia, and sesbania) have significant potential as fiber resources for energy application in general and for AJF production specifically. Furthermore, sugarcane is a good feedstock for producing alternative jet fuel in Hawai'i and the tropics via the alcohols to hydrocarbon and/or direct sugars to hydrocarbon pathways.

For most of the crops included in this review, there is generally insufficient information in the open literature detailing their performance and behavior undergoing conversion processes relevant to AJF production. Fundamental

Table 45. Summary of the State of Development of Feedstock-Technology Combinations for the Production of Jet Fuel from Tropical Biomass[a]

	TC pretreat	gasification	fast pyrolysis	HTL	hydrolysis pretreat	hydrolysis sugars	other alcohol	HTL	HRJ/HEFA
eucalyptus	na	2–3	2	1	1–2	1–2	0	1	
leucaena	na	1	1	0	1	1	0	0	
rice husks	2	2	2	1	1	1	0	1	
rice straw	2	2	3	1	2	2	1	1	
bagasse	na	3	2–3	1	2	2–3	1–2	1	
energycane	1	1	1	0	0	0	0	0	
banagrass	2	1	1	1	1	1	0	1	
sorghum	0	0	0	1	0	0	0	1	
sesbania	0	0	0	0	0	0	0	0	
glyricidia	0	0	0	0	0	0	0	0	
sugarcane						3[c]			
jatropha									1
pongamia									0[b]
kamani									0
croton									0

[a] 0 = no publications identified; 1 = preliminary research; 2 = extensive research; 3 = pilot or greater scale. na, not applicable. [b] Although no publication for production of hydrotreated pongamia oil was identified, there are numerous reports for production of FAME. [c] The production of alcohol via fermentation of sugar from sugarcane is a commercial process.

information such as mass and energy balances or production costs are notably absent. Table 45 provides an overview of the state of development of the feedstock-technology combinations assessed in this study. As information shortfalls are addressed across experimental scales (e.g., test tube, bench-scale, process development unit, demonstration scale, etc.), it is imperative that researchers design experiments, acquire data, and report results on bases that support process design and evaluation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.8b03001.

> Section S1, fuel properties and pretreatment methods; section S2, gasification; section S3, pyrolysis; and section S4, terminology (energy and efficiency) (PDF)

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Notes

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■ LIST OF ACRONYMS

AJF = alternative jet fuels
GHG = greenhouse gas
ASTM = American standard test method
CAS = Chemical Abstracts Service
FAA = Federal Aviation Administration
HEFA-SPK = hydroprocessed ester and fatty acids synthetic paraffinic kerosene
FT-SPK = Fischer–Tropsch-synthetic paraffinic kerosene
FT-SKA = Fischer–Tropsch-synthetic kerosene with aromatics
DSHC = direct sugars to hydrocarbons
SIP = synthesized iso-paraffins
ATJ = alcohol to jet fuel
HDCJ = hydrotreated depolymerized cellulosic jet
SK and SAK = synthetic kerosene and synthetic aromatic kerosene
CH = catalytic hydrothermolysis
PY = fast pyrolysis
HTL = hydrothermal liquefaction
HEFA = hydrotreated esters and fatty acids
HRJ = hydrotreated renewable jet fuel
DM = dry matter
daf = dry ash free
HPWRA = Hawai'i-Pacific Weed Risk Assessment
GAEZ = global agro-ecological zones
FFA = free fatty acids
FAME = fatty acid methyl esters

MSP = minimum selling price
GGE = allons of gasoline equivalent
Mg = mega grams
GJ = giga Joules
MJ = mega Joules
LCA = life cycle analysis
wt % = weight percent
TEA = techno-economic assessment
GTL = gas to liquid
bbl/day = barrels per day
MW_{th} = mega Watt thermal
NREL = National Renewable Energy Laboratory
LT = low temperature
HT = high temperature
MM = million
ppmv = parts per million by volume
EFB = empty fruit bunches
HNEI = Hawai'i Natural Energy Institute
S/B = steam to biomass ratio
CL = calcined limestone
CD = calcined dolomite
Nm^3 = normal meters cubed
DDG = distillers dried grain
ER = equivalence ratio air-to-fuel
LHV = low heating value
HHV = higher heating value
a.r. = as received
ESP = electrostatic precipitator
M.C. = moisture content
CFB = circulating fluidized bed
BFB = bubbling fluidized bed
EFG = entrained flow gasification-FT
TOP = torrefied and pelletized biomass
OW = operation window
NABC = national advanced biofuels consortium
LHSV = liquid hourly space velocity
WHSV = weight hourly space velocity
GHSV = gas hourly space velocity
MFSP = minimum fuel selling price
MSP = minimum selling price
MJSP = minimum jet fuel selling price
MESP = minimum ethanol selling price
HDS = hydrogen donor solvent
MSW = municipal solid waste
kWh = kilo Watt hour
kPa = kilo Pascal
GVA = gamma-valeroacetone
ABE = acetone-butanol-ethanol method
MTG = methanol-to-gasoline
VD = vacuum distillation
BIGCC = biomass integrated gasification with combined cycle
$Eff_{N\text{-}FB}$ = net fuel based efficiency
$Eff_{G\text{-}FB}$ = gross fuel based efficiency
$Eff_{N\text{-}PB}$ = net fuel process efficiency
$Eff_{N\text{-}PB}$ = gross fuel process efficiency

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Review of Biomass Resources and Conversion Technologies for Alternative Jet Fuel Production in Hawai'i and Tropical Regions

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Supporting Information

Supporting Information S1

Fuel Properties and Pretreatment Methods

Feedstock Properties:

The crops examined in this report are listed below, with tables summarizing their fuel properties and effect of pretreatment on those properties in the following sub-sections:

Fiber Crops:

1) Sugarcane bagasse *(Saccharum officinarum L.)*.
2) Energycane (type II - *Saccharum officinarum* X *S. rubustom*), fiber variety.
3) Banagrass *(Pennisetum purpureum x Pennisetum glaucum)*.
4) Leucaena-hybrid (*Leucaena*-KX4).
5) Eucalyptus (*Eucalyptus*, various species).
6) Rice husks/hulls (*Oryzae sativa* L.*)*.
7) Rice straw (*Oryzae sativa* L..*)*
8) Sorghum (*Sorghum bicolor* L.*)*, fiber variety.
9) Sesbania (*Sesbania grandiflora* (L.) Poir)
10) Glyricidia / gliricidia (*Gliricidia sepium* (Jacq.) Kunth ex Walp.*)*.

Oil Crops:

11) Jatropha (*Jatropha curcas* L.)
12) Kamani (*Calophyllum inophyllum* L.)
13) Pongamia (*Pongamia pinnata* (L.) Pierre)
14) Croton (*Croton megalocarpus* Hutch.)

Sugar Crops:

15) Sugarcane (*Saccharum officinarum* L.)

Fuel Properties Fiber Crops:

The chemical properties of the fiber crops (crops 1-8) are listed in Table S1.1 and S1.2 below. The data on leucaena, eucalyptus, sugarcane bagasse, energycane, pretreated energycane (S3), banagrass and pretreated banagrass (S3) are for crops grown in Hawaii, details of the growing conditions and locations can be found elsewhere [1]. Data for sorghum, rice husks and rice straw are complied from various literature sources, i.e. properties are from reports by different researchers using different samples of sorghum, rice husk or straw, hence the values are given as ranges [2-7]. There is limited information on the fuel properties of crops 9 &10 (sesbania and glyricidia). The only data indentified was for glyricidia; ash content (db) 0.04 wt%, volatiles 82.1 wt% and fixed carbon 17.8 wt% [8].

With regard to energycane, there are different varieties that have been grown in Hawaii that have varying amounts of sugar and fiber. Type II energycane contains low sugar and high fiber content with sub-species having different sugar and fiber contents; fiber content ranges from 12.5 to 16.0 wt% (wet basis) and sugar content from 5.2 to 5.4 wt% (wet basis). Type I sugarcane has a lower fiber content and higher sugar content (fiber 13.5 wt% and sugar 10.4 wt%, wet basis). The fuel properties listed in Table S1.1 are for type II energycane with 16 wt% fiber and 5.2 wt% sugar (wet basis), type I energycane is *not* included in this report.

Table S1.1. Fuel properties of leucaena, eucalyptus, sugarcane bagasse, energycane, banagrass, sorghum, rice husks and rice straw [1-6, 9-13].

	Leucaena	Eucalyptus	Bagasse	E-Cane	Banagrass	Rice Husk [2, 3, 14, 15]	Rice Straw [3-6, 16, 17]	Sorghum [4, 7]
Proximate analysis (wt% dry basis)[β]								
Ash	0.9-7.2	0.7	4.2-7.6	6.6	8.5	12.8-22.0	14.8-20.1	4.2-5.5
Volatiles	74.3-83.2	86.3	79.2-82.4	78.7	83.3	63.0-74.0	61.6-66.7	75.0-81.6
Fixed C	15.3-18.5	13.0	10.0-14.9	14.7	8.3	13.2-19.2	12.8-15.6	14.2-19.5
SUM	100.0	100.0	100.0	100.0	100.1	100	100.0	100.0
Heating values (MJ/kg dry basis)								
HHV	18.9-19.5	18.4	18.0	17.1	16.8	16-17	15.1-18.5[α]	16.1
LHV	17.6	17.1	16.8	15.9	15.7	14-15	14.0-17.3[α]	-
Ultimate analysis (wt% dry-ash-free basis)[β]								
Carbon	49.8-53.1	50.3	49.2-51.7	50.4	51.1	45.0-49.3	36.5-50.1	40.7-49.4
Hydrogen	6.0-6.1	6.0	5.6-6.0	5.9	5.7	5.6-7.0	5.6-7.0	6.3-6.4
Nitrogen	0.24-0.31	0.1	0.1-0.7	0.4	0.5	0.6-1.3	0.9-1.3	0.3-0.5
Sulfur	0.02-0.24	0.05	0.04-0.05	0.32	0.11	0.05-0.08	0.13-0.53	0.05-0.2
Oxygen*	38.8-43.7	43.5	38.6-45.0	42.6	41.2	43.0-48.9	29.3-44.6	44.0-52.2
Chlorine	0.09-0.13	0.06	0.02-0.71	0.3	1.3	0.1-0.2	0.31-0.58	0.04
SUM	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Compositional analysis (wt% dry-ash-free basis)[ε]								
Lignin	28.0	26.7	25.5	22.7	23.5	22.6	13.5-16.5	-
Cellulose	41.5	43.7	39.2	37.0	35.5	40.3	37.5-47.4	-
Hemicellulose	12.8	9.9	20.2	14.7	17.5	29.1	24.3-29.7	-
SUM	82.2	80.3	84.9	74.4	76.5	92.0	78.0-90.7	-

Moisture content of the biomass samples after grinding to <200 µm particle size
*Oxygen by difference
[α] Rice Straw data from the ECN 'phyllis2' database for Rice Straw sample #2001.
[β] Standard deviation is estimated to be < 0.5 wt% of the absolute values
[ε] Relative standard deviation is < 10 %.

The woody biomass and bagasse have the highest lignin contents, while energycane, banagrass and rice husks have intermediate lignin content. Rice husks have a similar cellulose, hemicellulose and lignin content as beech wood [3]. Rice straw has the lowest lignin content and the greatest cellulose content. Fixed carbon from rice husks is at the higher end of the range seen for biomass species. Volatile matter from rice husks and rice straw is lower than woods and grasses. The ash content of rice husks and rice straw are much higher than most types of biomass (woods, grasses and nut shells, etc.). The grasses and bagasse have intermediate ash contents, which can be considered as high in comparison to woody biomass. The ash composition of crops 1-8 are provided later in this appendix.

Feedstock Pretreatment and Leaching (for thermochemical conversion):

All types of biomass require some form of 'pretreatment' or 'pre-processing' before it can be used in a thermochemical process. Woody biomass samples require particle size reduction and drying (ideally to ~10 wt% moisture for gasification and pyrolysis). Grasses such as banagrass and energycane require an additional dewatering step after particle size reduction and may also require leaching to remove inorganic components which are present in high levels in these feedstocks. Leaching of rice straw and husks has also been studied due to their high ash content. The fuel properties of leached feedstocks are provided in Tables S1.2 and S1.3.

The chemical composition of biomass is highly dependent on the growing conditions (soil, fertilizer, etc.) and the type (species) of biomass. This is particularly important regarding the biomass ash content and inorganic composition. Some inorganic components in biomass cause problems during thermochemical conversion (typically K, Na, Cl and S). Therefore, depending on the conversion technology used the feedstock may require leaching to remove problem elements prior to processing. In this context 'leaching' refers to washing / soaking the biomass in water, acidic or basic solution to remove certain inorganics [9, 14, 16, 18-20].

A moisture content of 70 % (wet basis) is typically for fresh herbaceous crops (banagrass, energycane) [10, 18]. Dewatering of banagrass has been previously examined using sugar-processing technology to reduce its moisture content and remove alkali and alkali earth metals (AAEM) [10, 18]. Two methods were compared i) using sugar-processing technology where a forage chopper reduces the particle size to ~4 mm (average) followed by pressing; and ii) a Jeffco cutter which reduces the particle size to ~ 2mm (average) before pressing. The pressing step (using a screw press) dewaters the sample from ~70 % (wet basis) to ~50% moisture and removes some inorganic species. Table S1.2 shows the fuel properties of energycane S3 and banagrass S3 (S3 refers to pretreatment using pressing-water leaching-pressing), and for rice husks and rice straw after being leached with water or an acid. Table S1.3 lists the fuel properties of banagrass after four type of pretreatment, see the footnotes in the table for details [10, 18]; note: the four pretreated banagrass samples were used in air-blown gasification tests [10], however those results are not discussed in this report as the producer gas is not suited to production of jet fuel.

Leaching with water is the preferred method due to cost. For banagrass, leaching with water can remove 50-60 wt% of the Na, ~65 wt% Mg, ~90 wt% P, ~90 wt% K, ~55 wt% S, and ~95 wt% Cl [1] (and *paper in preparation - Morgan & Turn, HNEI*). Extraction efficiencies for energycane (water leaching) are similar to those for banagrass [1]. For rice husks or straw, water leaching removes ~70-80 % of K and Na, ~55 % Fe, ~33-45 % Mg and ~17-36 % Ca [14, 16]. The inorganics that cannot be removed by water are organically bound species in carboxylates or in inorganic minerals which require leaching in an acidic medium [14, 16]. Acid leaching can typically remove >90% of the K, Na and Mg, and ~50 % of Ca [14, 16].The ash composition of crops 1-8 before and after pretreatment are listed in Tables S1.4, S1.5 and S1.6.

It should be noted that the use of mineral acids (HCl, H_2SO_4) is not practical in an industrial application due to contamination of the sample with Cl and S. Organic acids (acetic acid) are considered more viable but may prove too expensive, hence there has been research into the use of acetic acid derived from biomass pyrolysis oil (or using a fraction of the pyrolysis oil) as a leachate [14]. However the use of biomass pyrolysis oil to leach biomass introduces other issues which require further research before it can be considered a practical approach.

Table S1.2. Fuel properties of pretreated (leached) energycane S3, banagrass S3, rice husks and rice straw [1, 5, 6, 16, 20].

	E-Cane S3	Banagrass S3	Rice Husk Leached [a]	Rice Husk Leached [b]	Rice Straw leached [c]	Rice Straw leached [d]
Moisture[#] wt%	5.6	0.5[α]	-	-	7.0-9.0	7.0
Proximate analysis (wt% dry basis)[β]						
Ash	3.2	5.1	8.0	18.7	9.9-22.0	7.8
Volatiles	86.4	84.6	-	-	69.4	71.6
Fixed C	10.4	10.4	-	-	13.5	13.9
SUM	100.0	100.0	-	-	100.0	100.0
Heating values (MJ/kg dry basis)						
HHV	18.6	18.5	-	-	14.9	-
LHV	17.4	17.2	-	-	13.9	-
Ultimate analysis (wt% dry-ash-free basis)[β]						
Carbon	53.0	52.3	43.0	38.0	45.0-48.7	48.4
Hydrogen	5.9	6.0	6.0	5.3	5.7-6.1	6.2
Nitrogen	0.3	0.2	2.7	1.9	0.7-0.8	0.9
Sulfur	0.05	0.03	-	-	0.15-0.17	0.2
Oxygen*	40.7	41.4	40.6	36.1	41.5-44.4	44.2
Chlorine	0.01	0.03	-	-	0.01	-
SUM	100.0	100.0	-	-	100.0	100.0
Compositional analysis (wt% dry-ash-free basis)[ε]						
Lignin	26.9	22.5	-	-	-	-
Cellulose	36.3	36.9	-	-	-	-
Hemi-cellulose	17.3	18.1	-	-	-	-
SUM	80.5	77.5	-	-	-	-

Moisture content of the biomass samples after grinding to <200 µm particle size
*Oxygen by difference
[a] Leached with water [20]
[b] Leached with acid (HCl) [20]
[c] Leached with water [5, 6, 16]
[d] Leached with acetic acid [16]
[α] Banagrass S3, this sample was oven dried to aid grinding.
[β] Standard deviation is estimated to be < 0.5 wt% of the absolute values
[ε] Relative standard deviation is < 10 %.
Data for the leached rice straw is for the same batch of straw as reported in Table S1.5

Table S1.3. Fuel properties of banagrass after size reduction and pretreatment (leaching) by various methods [10, 18].

	Banagrass JC-PRP	Banagrass FC-PRP	Banagrass FC-P	Banagrass FC-UP
Moisture[#] wt%	11.4	7.1	7.1	8.4
Proximate analysis (wt% dry basis)[β]				
Ash	3.8	3.0	4.1	4.5
Volatiles	80.6	81.5	79.4	78.2
Fixed C	15.7	15.5	16.5	17.3
Heating values (MJ/kg dry basis)				
HHV	18.5	18.7	18.5	18.3
LHV	-	-	-	-
Ultimate analysis (wt% dry-ash-free basis)[β]				
Carbon	48.9	48.9	48.9	49.3
Hydrogen	5.3	5.4	5.3	5.5
Nitrogen	0.23	0.37	0.46	0.46
Sulfur	0.04	0.14	0.15	0.17
Oxygen*	45.5	45.2	44.8	43.9
Chlorine	0.03	0.11	0.33	0.64
Compositional analysis (wt% dry-ash-free basis)[ε]				
Lignin	-	-	-	-
Cellulose	-	-	-	-
Hemi-cellulose	-	-	-	-

Moisture content of the biomass samples after grinding to <200 µm particle size

*Oxygen by difference

[β] Standard deviation is estimated to be < 0.5 wt% of the absolute values

[ε] Relative standard deviation is < 10 %.

JC-PRP Jeffco cutter pressed-leach-press; FC-PRP forage chopper pressed-leach-press; FC-UP forage chopper unpressed; FC-P forage chopper pressed

Table S1.4. Elemental analysis of the ash from leucaena, eucalyptus, sugarcane bagasse, energycane, banagrass, sorghum, rice husks and rice straw. The ash was calcined at 600 °C prior to analysis. Presented as wt% of the dry feedstock [1, 10, 18].

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3	Cl	CO_2
Leucaena	0.3	0.1	0.002	0.11	0.4	0.1	0.03	0.3	0.1	0.01	0.10	0.1
Eucalyptus	0.02	0.02	0.001	0.04	0.2	0.04	0.04	0.1	0.1	0.01	0.01	0.1
S-bagasse	2.5-3.0	1.4-1.6	0.15-0.30	1.0-1.5	0.1-0.2	0.10-0.12	0.03-0.10	0.2	0.08-0.10	0.03-0.10	<0.01	0.02
E-Cane	4.1	0.1	0.001	0.03	0.4	0.1	0.1	0.9	0.2	0.5	0.20	0.02
Banagrass	4.0	0.1	0.001	0.04	0.2	0.2	0.04	2.3	0.5	0.1	1.00	0.1
Rice Husk [2, 3, 14]	11.2-17.0	0.04	0.004	0.01-0.04	0.17-0.21	0.04-0.10	0.03-0.05	0.41-0.69	0.09-0.47	0.04-0.08	0.1-0.2	0.1
Rice Straw [4-6]	13.2-15.5	0.01-0.11	0.01	0.040.10	0.30-0.49	0.27-0.54	0.08-0.36	2.53-3.04	0.20-0.34	0.16-0.24	0.21-0.58	0.1
Sorghum [4, 7]	3.07	0.08	<0.01	0.04-0.09	0.29-0.31	0.09-0.15	0.01-0.05	0.38-0.51	0.09-0.19	0.05-0.12	-	-

Table S1.5. Elemental analysis of the ash from pretreated energycane (S3), banagrass (S3), rice husks and rice straw. The ash was calcined at 600 °C prior to analysis. Presented as wt% of the dry feedstock [1, 10, 18].

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3	Cl	CO_2
E-Cane S3	2.1	0.04	0.003	0.06	0.1	0.03	0.02	0.1	0.05	0.05	0.001	0.01
Banagrass S3	3.1	0.1	0.001	0.09	0.2	0.1	0.03	0.3	0.1	0.04	0.02	0.1
Rice Husk Leached (WS) [14]	-	-	-	-	0.13	0.05	0.02	0.16	-	-	-	-
Rice Husk Leached (WS-AAS) [14]	-	-	-	-	0.08	0.01	0.003	0.02	-	-	-	-
Rice Straw leached [5, 6] (#2001)	18.1	0.97	0.06	0.53	0.54	0.36	0.14	0.44	0.17	0.09	0.01	0.05
Rice Straw leached (acetic acid) [16]	-	-	-	0.02	0.38	0.02	0.01	0.02	-	-	-	-
WS, leached using water (water soluble) WS-AAS, leached with water followed by ammonium-acetate solution #2001 is the ID for the sample in the ECN Phyllis2 database, leached with rain water in the field.												

Table S1.6. Elemental analysis of the ash from banagrass after size reduction and pretreatment (leaching) by various methods [10, 18]. The ash was calcined at 600 °C prior to analysis. Presented as wt% of the dry feedstock.

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3	Cl	CO_2
Banagrass JC-PRP	2.3	0.31	0.03	0.14	0.33	0.08	0.03	0.21	0.06	0.06	<0.01	0.03
Banagrass FC-PRP	1.7	0.02	<0.01	0.03	0.30	0.12	0.02	0.45	0.10	0.04	0.07	0.02
Banagrass FC-P	2.0	0.04	<0.01	0.04	0.35	0.21	0.03	1.0	0.15	0.09	0.24	0.01
Banagrass FC-UP	1.7	0.04	<0.01	0.05	0.27	0.23	0.04	1.5	0.16	0.07	0.50	0.01

JC-PRP Jeffco cutter pressed-rinse-press; FC-PRP forage chopper pressed-rinse-press; FC-UP forage chopper unpressed; FC-P forage chopper pressed

The main problem elements in biomass in regard to thermochemical processing are alkali and alkali earth metals (AAEM: K, Na, Ca and Mg), as well as Cl, and S. These elements can cause deposition, bed agglomeration and corrosion problems (i.e. during gasification or pyrolysis) and/or adversely affect downstream processes such as poisoning catalysts used for upgrading [9, 10, 13, 18]. In addition, Si and K (or other AAEM) can combine in eutectic mixtures which have low melting points (~800 °C) which cause issues in combustion and gasification processes. High levels of AAEM in biomass can also influence reaction pathways during thermochemical processing, resulting in reduced pyrolysis oil yields which appears to be due to increased cracking of primary oil/tars [1, 19, 21, 22].

Note: not all species of biomass will require pretreatment, for example tree species such as leucaena and eucalyptus typically have low ash contents (less than 2 wt% of the dry feedstock) and relatively low amount of problem species (AAEM, Cl, S). Therefore, the decision as to which biomass species to pretreatment is based on the chemical composition of the biomass, the process used to produce jet fuel, and the cost of the pretreatment process relative to the advantages gained through pretreating the feedstock.

Fuel properties for feedstocks used by other research cited in this report:

Table S1.7. Ultimate and proximate analysis of feedstocks examined by steam-O_2 gasification, reproduced from Su et al., [23]. Gasification results for these feedstocks are reported in Table 22, Section 3.2.1.3.

Feedstock	Moisture	Ultimate Analysis					Proximate Analysis (dry wt.%)			HHV
Feedstock	wet (%)	C	H	O	N	S	V	FC	A	(MJ/kg)
Sawdust A	10.4	45.9	5.4	47.8	0.1	0.0	82.1	17.1	0.8	17.6
Sawdust B	13.2	48.8	5.8	44.3	0.0	0.0	82.8	16.1	1.1	17.8
Straw	11.2	41.0	5.6	39.4	3.9	0.1	70.9	19.1	10.0	16.6
Corncob	6.8	44.4	5.3	43.0	2.4	0.1	78.4	16.8	4.8	17.1
Rice Husk A	10.3	38.3	5.1	43.1	1.7	0.2	67.5	20.8	11.7	14.7
Rice Husk B	9.7	42.3	5.9	39.9	0.5	0.3	70.1	18.8	11.1	17.8
Wood Pellets A	6.3	53.5	5.9	39.6	0.1	0.0	82.4	16.7	0.9	21.7
Wood Pellets B	7.2	44.6	8.5	40.8	3.5	0.5	77.8	20.1	2.1	19.3
Straw Pellets	6.8	43.2	5.7	35.9	3.7	0.2	68.7	20.0	11.3	17.3
RDF A	5.9	61.6	9.9	20.2	0.0	0.2	85.1	6.8	8.1	31.1
RDF B	5.7	53.6	7.7	34.0	0.0	0.3	88.5	7.1	4.4	24.2

Fuel Properties of Oil Crops:

The raw oils yields from the seeds or fruits of the oil crops (jatropha, pongamia, kamani and croton) are typically in the range of 25 to 35 wt%, although higher yields have been reported (up to 75 wt% dry basis) depending on the extraction method used [24, 25]. The yield of seeds or fruits are ~4.8 tonnes per hectare per year for pongamia and kamani, ~6.5 t ha^{-1} yr^{-1} for jatropha and ~14 t ha^{-1} yr^{-1} for croton. Fatty acid profiles of the oil recovered from the four seeds are presented in Tables S1.8 and S1.11.

Table S1.8. Fatty acid profiles for *Jatropha curcas*.

Fatty acid (# of C atoms: # of double bonds)	Jatropha							
	--------*Jatropha curcas*--------							
Capric (10:0)								
Lauric (12:0)								0.14
Myristic (14:0)		0.18	0.15	1.18	0.3		1.4	0.11
Palmitic (16:0)	18.5	11.4	12.3	13	10.5	19.5	15.6	16.64
Palmitoleic (16:1)		0.44	0.55	0.52	0.32			1.18
Heptadecanoic (17:0)								
Stearic (18:0)	2.3	2.27	2.8	2.53	2.45	6.8	9.7	5.94
Oleic (18:1)	49.0	45	47.1	48.8	41.5	41.3	40.8	37.25
Linoleic (18:2)	29.7	40.3	26.7	34.6	44.4	31.4	32.2	38.03
Linolenic (18.3)		0.11	0.18	0.12	0.21			0.25
Arachidic (20:0)							0.4	0.46
Eicosenoic (20:1)		0.12	0.19	0.14	0.14			
Eicosadienoic (20.2)		0.11	0.11	0.1	0.13			
Behenic (22:0)								
Erucic (22:1)								
Lignoceric (24:0)								
Total Saturated	20.8	13.85	15.25	16.71	13.25	26.3	27.1	23.29
Total Unsaturated	78.7	86.08	74.83	84.28	86.7	72.7	73	76.71
Reference	[26]	[27]	[27]	[27]	[27]	[28]	[29]	[30]

Table S1.9. Fatty acid profiles for *Croton megalocarpus*.

Fatty acid (# of C atoms: # of double bonds)	Croton			
	-----------*Croton megalocarpus*-----------			
Capric (10:0)				
Lauric (12:0)				0.11
Myristic (14:0)	0.1	0.1		0.04
Palmitic (16:0)	6.5	7.2	7.4	6.23
Palmitoleic (16:1)	0.1			0.11
Heptadecanoic (17:0)	0.1			
Stearic (18:0)	3.8	3.7	4.1	4.37
Oleic (18:1)	11.6	13.7	12.2	9.95
Linoleic (18:2)	72.7	69	71.2	74.31
Linolenic (18.3)	3.5	4.6	3.4	3.62
Arachidic (20:0)				0.92
Eicosenoic (20:1)	0.9	0.1	0.9	
Eicosadienoic (20.2)	0.2			
Behenic (22:0)				
Erucic (22:1)				0.33
Lignoceric (24:0)				
Total Saturated	10.5	11	11.5	11.67
Total Unsaturated	89	87.4	87.7	88.32
Reference	[31]	[32]	[33]	[30]

Table S1.10. Fatty acid profiles for *Milletia pinnata*.

Fatty acid (# of C atoms:# of double bonds)		Pongamia -----------*Milletia pinnata*-----------	
Capric (10:0)		0.1	
Lauric (12:0)		0.1	
Myristic (14:0)			
Palmitic (16:0)	7.18	10.8	11.3
Palmitoleic (16:1)			
Heptadecanoic (17:0)			
Stearic (18:0)	3.32	8.7	12.9
Oleic (18:1)	43.99	46	41.4
Linoleic (18:2)	17.38	27.1	26.7
Linolenic (18.3)	5.51	6.3	
Arachidic (20:0)	0.78	0.8	
Eicosenoic (20:1)	3.43		
Eicosadienoic (20.2)			
Behenic (22:0)	2.48		
Erucic (22:1)	15.9		
Lignoceric (24:0)			
Total Saturated	13.76	20.5	24.2
Total Unsaturated	86.21	79.4	68.1
Reference	34	35	36

Table S1.11. Fatty acid profiles for *Calophyllum inophyllum*.

Fatty acid (# of C atoms:# of double bonds)	Kamani ----------------------*Calophyllum inophyllum*----------------------				
Capric (10:0)					
Lauric (12:0)			0.1		
Myristic (14:0)			0.1		
Palmitic (16:0)	13.7	15.4	14.2	17.1	15.6
Palmitoleic (16:1)	0.2		0.3		
Heptadecanoic (17:0)					
Stearic (18:0)	14.3	13.7	15.9	8.3	15.9
Oleic (18:1)	39.1	35.7	39.8	47.1	30.1
Linoleic (18:2)	31.1	34.3	28.1	27.1	38.4
Linolenic (18.3)	0.3	0.1	0.2		
Arachidic (20:0)	0.6		0.8		
Eicosenoic (20:1)	0.1	0.2			
Eicosadienoic (20.2)					
Behenic (22:0)	0.2				
Erucic (22:1)					
Lignoceric (24:0)	0.2				
Total Saturated	29	29.1	31.1	25.4	31.5
Total Unsaturated	70.8	70.3	68.4	74.2	68.5
Reference	37	38	39	40	41

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Supporting Information S2

Gasification

Gasification Reactors and FT Synthesis:

There are three main types of gasifier suitable for processing biomass 1) fixed-bed or moving bed designs, 2) fluidized-bed, and 3) entrained flow configurations. A brief description of each reactor system is provided below.

Fixed-bed (moving bed) gasifier: Updraft/downdraft gasifiers are attractive for small scale applications (<1.5 MW_{th} input). Scale-up can be realized by parallel operation of multiple units. For this type of gasifier, fuel particle size should be controlled within a consistent range that allows uniform gas flow through the bed. Thus, certain types of grass fuels with low bulk density (such as straw) must be pelletized prior to gasification. In addition, efficient tar removal is always a problem for a small scale industrial application.

Updraft gasifiers are characterized by biomass entering the top of the reactor and air and/or oxygen and/or steam entering from the bottom of the reactor. The flow of gas and the movement of the reaction zone in the reactor are co-current with the product gas leaving from the top of the reactor. In this reactor, tars form at a level of up to 100 g/Nm^3 [1]. Advantages of updraft gasifiers include a mature technology for heat production for small-scale applications with a high carbon conversion and high tolerance for elevated moisture content. Noteworthy disadvantages are that the fuel particle size must be within certain limits, high tar yields and the potential for slagging [2]. In addition, the composition and yield of the producer gas is not ideal for FT-synthesis of hydrocarbons.

Downdraft gasifiers are characterized by biomass entering at top of the reactor with air, steam or oxygen added through the throat of the reactor. Product gas exits at the bottom of the reactor, the propagation of the reaction zone and the gas flow are in opposite directions or counter-current. The product gas contains low concentration of particulates and tars (approximately 1 g/Nm^3). Most of the tars are combusted or cracked in the reactor throat region at temperatures between 1000-1400°C. This reactor is preferred when clean gas is desired. Disadvantages of this reactor type include a lower overall thermal efficiency, poor quality synthesis gas, and difficulties in handling biomass with higher moisture and ash contents [2].

Commercial fixed bed gasifier manufacturers include Lurgi Dry-Ash Gasifier, and BGL Gasifier. Both were initially designed for coal gasification but were modified to use biomass. For small and medium scale gasifier systems, an inventory of US manufactures can be found in a NREL technical report [3].

Fluidized-bed gasifier: In a fluidized-bed gasifier, biomass fuels with particle sizes up to 10 cm enter at the bottom of the reactor along with air, oxygen or steam (or combinations). The velocity of the gas stream forces the biomass upward through a hot bed of fluidized particles (inert materials such as ceramic or silica, or catalytic materials, such as olivine, can be used). In general, fluidized bed gasifiers can accept a wide variety of feedstocks, and the operating temperature should be lower than the ash melting temperature of the fuel, commonly between 700°C and 1100°C. This type of gasifier produces considerable amounts of tar and aromatics, which requires extensive gas cleaning. The typical tar concentration is 10 g/Nm^3 which falls in the range between the updraft and the downdraft gasifier [1]. Fluidized bed gasifiers are best suited for large-scale applications of up to several hundred MW$_{th}$ fuel input. There are two main designs of fluidized-bed gasifiers (i) a bubbling fluidized-bed gasifier (BFBG) and (ii) a circulating fluidized-bed gasifier (CFBG).

Fluidized-bed gasifiers have proven to be reliable at both pilot and commercial scales. BFBG are more economic for small to medium range (1-10 MW$_{th}$ fuel input) capacities, whereas CFBG are very reliable for a variety of fuels and are relatively easy to scale up to at least 100 MW$_{th}$ fuel input [4].

Pressurized reactors can increase the system capacity and can benefit an integrated combined cycle (such as IGCC, and FT synthesis) as the product gas has to be pressurized before entering the combustion chamber of a gas turbine or a FT synthesis reactor. However, pressurized systems incur additional capital costs.

Fluidized bed gasifiers are commercially manufactured by HTW (High Temperature Winkler), KBR Transport Gasifier, Great Point Energy and U-GAS [5]. Most are currently designed and used for coal gasification. For small and medium scale biomass gasification systems, a number of the US companies can be found in a NREL report [3].

Twin-bed fluidized-bed gasifier: A twin fluidized-bed, indirectly-heated gasifier system consists of a fluidized-bed combustor and a fluidized-bed gasifier. In this coupled system, biomass is typically reacted with steam in the gasifier and char is reacted with air in the combustor. Char, together with sand (bed material), is circulated from the gasifier to the combustor, where char and any carryover gases are burned using air [6]. Thermal energy is provided to the gasifier by circulating hot sand from the combustor to the gasification reactor. As a result, sand is circulated between the two reactors and transfers heat from the combustor to the gasifier. Moreover, the gas produced in the gasifier is nearly free of nitrogen since this system keeps the flue gas separate from the gasifier, producing a good quality producer gas better suited for FT synthesis.

The Battelle gasification process, demonstrated at the McNeil power plant in Burlington, Vermont, is an example of an indirectly heated gasifier that generated producer gas from biomass. The primary fuel gas was of medium calorific value with a HHV of 17.75 MJ/Nm^{3}[4]. A commercial indirectly heated gasifier plant has been operating since 2003 in Gussing, Austria [7]. This biomass CHP plant has a capacity of 8 $\mathrm{MW_{th}}$ fuel input and outputs of 2 MW electricity combined with 4.5 MW thermal and includes a demonstration scale FT synthesis reactor.

Choosing an allothermal twin-bed gasifier with coupled FT synthesis for liquid fuels production can avoid the large capital investment for an air separation unit (ASU) for oxygen production which is required for oxygen blown designs. Compared with the other gasifiers, a twin-bed gasifier is more complex to build [8], but can realize a higher energy conversion efficiency [9].

Entrained Flow Gasifier: The entrained flow gasifier differs significantly from the fixed-bed and fluidized-bed gasifiers described previously. It requires feedstock with very small particle size (~1 mm) or a pumpable liquid phase (water/biomass slurry, or bio-oil/char slurry [10, 11]), that enters with oxygen and steam at the top of the gasifier.

Typically, an entrained flow gasifier is operated at high pressure (up to 100 bar) and high temperature (up to ~1400°C) and completely converts the feedstock into producer gas, even at short residence times (a few seconds). An external pilot flame (often using natural gas) may be required to increase temperature and to facilitate reactions. Under these conditions, the producer gas contains very low level of tar and methane, which simplifies gas cleaning and increases efficiency for the subsequent FT synthesis processes.

An entrained flow gasifier can be used for biomass feedstocks with low ash melting points. A fluxing material can be added, such as limestone or other Ca-rich material, to enhance ash conversion to molten slag. Molten slag condenses and forms a solid protective layer on the inner wall of the gasifier. The molten slag remains in liquid form as it flows down the gasifier and exits at the bottom [6].

In comparison to fixed-bed and fluidized-bed gasifiers, an entrained flow gasifier is capital intensive and requires larger fuel throughput to take advantage of economies of scale and limit production costs. Therefore, entrained flow gasifiers are considered economical at scales of ~1000 MW_{th} fuel input [2, 6, 12].

Manufacturers of slagging entrained flow gasifiers include Shell, GE (former Texaco), Krupp-Uhde, ConocoPhillips (E-Gas™), Siemens, MHI (Mitsubishi Heavy Industries), Huaneng Clean Energy Research Institute (HCERI). Most are designed for coal gasification but can be modified to use biomass as feedstock [5].

FT Synthesis: FT synthesis has two main modes of operation [13]:

i) fixed bed slurry phase reactors for low temperature FT (LTFT) using Fe or Co based catalysts to produce linear long-chain alkanes ($>C_{10}$), i.e. diesel range (C_{12}-C_{20}) and waxes ($>C_{20}$);

ii) fluidized bed reactors operated at higher temperature (HTFT) with Fe-catalysts for production of short chain alkanes (C_2 to C_4), gasoline range alkanes (C_4 to C_{12}) plus some middle distillates (C_{10} to C_{20}) and waxes ($>C_{20}$). See Table S2.1 below for a more detailed breakdown of the product distributions from LTFT and HTFT.

Iron based catalysts can be used at low or high temperature to produce different products. LTFT with Fe-catalyst produces mostly high molecular mass linear alkanes and waxes ($>C_{12}$) and some gasoline range alkanes (C_4 to C_{12}). HTFT with Fe-catalyst produces mostly gasoline range alkanes and linear low molecular mass alkanes (C2-C12). Less common forms of FT synthesis involve the use of Ni based catalysts for the production of methane, or the incorporation of Cu into a Fe-based catalyst to produce methanol and higher alcohols [13].

The focus of this report is on the production of jet fuel. Jet fuel typically has a boiling point (BP) range of 150 to 290 °C and is composed of a blend of hydrocarbons typically C_8 to C_{16}, it is a middle distillate between gasoline and diesel. Therefore the best suited FT approach to jet fuel production is LTFT with a Fe based catalyst.

FT catalysts (Fe or Co based) are typically very sensitive to sulfur which can cause permanent poisoning of the catalyst, sulfur has to be removed from the producer gas before it enters the FT reactor to a level of <100 ppm [13]. Ammonia poisoning is also an issue for Co based FT catalysts. Producer gas also contains fine particulate matter, C_2+ gaseous hydrocarbons, heavier condensable hydrocarbons (benzene and higher molecular weight compounds) that are collectively termed “tar” and gaseous containments such as HCl, NH_3, HCN, as well as alkali metals that are vaporized during thermochemical conversion of biomass feedstocks. These contaminants are potentially damaging to catalysts and require removal prior to synthesis reactions.

In addition, CO_2, one of the by-products from gasification, often needs to be removed prior to the producer gas entering the compressor and pressurized synthesis reactors. Further details regarding gas cleaning can be found elsewhere [12], brief summaries of the key points are provided below.

Tar removal:A general definition of tar is that of a complex mixture of condensable hydrocarbons. The efficient and economic removal of tar still remains as a technical barrier for biomass gasification [1, 12, 14].The main methods used to eliminate tar include wet scrubbing, wet electrostatic precipitation, and catalytic reforming [14].

Sulfur and other gaseous impurities removal: Under the reducing atmosphere of gasification conditions, H_2S is the primary sulfur species produced when sulfur is present in the biomass feedstock. Minor amounts of carbonyl sulfide (COS), and thiophene (C_4H_4S) are also formed. These gaseous sulfur compounds deactivate catalysts used for tar cracking and the water-gas shift (WGS) reaction in downstream reactor units as well as catalysts used for FT synthesis.

Zinc oxide (ZnO) is the most commonly used sorbent for H_2S removal because of its favorable sulfidation thermodynamics. The removal of H_2S is accomplished by reacting ZnO and H_2S to produce ZnS and water. Before the producer gas can be used in FT synthesis sulfur has to be reduced to less 100 ppm, or to less than 1 ppm for mixed alcohols synthesis [13, 15].

Ammonia (NH_3) is the most significant species formed from fuel nitrogen in biomass gasification and is a precursor to NO_x emissions from downstream burners, gas engines, or gas turbines. NH_3 can be removed by wet scrubbing or catalytic conversion [16]. Ni-based tar-reforming catalysts operating at ~800°C have been shown to effectively remove NH_3 from gasifier product gas [16, 17].

Other trace contaminants, including cyanide and chloride compounds, may also cause corrosion and poison catalysts. Hence, efficient removal may be required.

Alkali removal: The mineral matter in biomass may contain high levels of alkali metals, notably potassium (K), that are released as alkali salts, typically as KCl, during gasification. Alkali vapors can deposit on cold surfaces downstream or condense onto particulate matter. Alkali removal from the gas stream is therefore important to protect critical downstream applications such as gas turbines [16].

Alkali vapor can be removed by cooling the product gas below 600 °C to condense it onto solid particulates. The particulate matter can be removed using various filtration systems, such as electrostatic filters, bag filters, or wet scrubbers. Ceramic or metallic barrier filters are not recommended due to the potential reactions with gas stream components. These systems require cooling of the product gas and the accompanying loss of sensible enthalpy that may reduce system efficiency. Alkali "getters" [18], a packed-bed filter loaded with sorbent material, may be an effective method to remove alkali from the gas stream at higher temperatures (650-725 °C).

Turn et al [19] reviewed sorbent materials for removal of alkali vapors at elevated temperature from producer gas. Alumina and silicate sorbents were examined. Activated bauxite, kaolinite, emathalite and diatomaceous earth were identified as potential candidates, however experimental data for these materials in an environment representative of biomass gasification was found to be lacking.

Synthesis of Liquid Fuels: Clean producer gas must be delivered to the FT synthesis reactor at pressures ranging from 20-200 bar, depending on the synthesis conditions [5]. In principle, if clean producer gas is produced from biomass, no serious technical barrier prevent its conversion to methanol, ethanol or FT liquids (gasoline, jet fuel, diesel) as these processes have been demonstrated or commercialized by Shell in Malaysia and SASOL in South Africa.

FT synthesis generates a distribution of products that depends on the catalysts and the reaction conditions. Table S2.1 lists the products from two types of FT synthesis performed at different temperatures using a Fe-based catalyst [20].

Table S2.1. FT products distribution for Fe-catalyst (per 100 carbon atoms) [20]

Products	Low temperature (220-250 °C)	High temperature (330-350 °C)
CH_4	4	7
C_2 to C_4 olefins	4	24
C_2 to C_4 paraffin	4	6
Gasoline (C_4 to C_{12})	18	36
Middle distillate (C_{10} to C_{20})	19	12
Heavy oil and waxes ($>C_{20}$)	48	9
Water soluble oxygenates	3	6

There are three types of FT reactor that have been applied commercially or are considered suitable for commercial application. These reactors are i) gas/solid - two phase - fluidized bed reactors, ii) the multi-tubular fixed bed reactors and iii) three phase slurry reactors [21]., There is insufficient background information, however, to prefer one reactor type over another [21].

The fluidized bed and the three phase slurry reactors have been applied extensively by Sasol (South Africa), while the multi-tubular fixed bed reactors were developed by Shell. The main advantages of the multi-tubular fixed bed and three phase slurry reactors are listed below (reproduced from [21]):

Multi-tubular fixed bed reactor:

- easy scale-up, hence no expensive demonstration unit necessary;
- no system needed for separation of catalyst and liquid product;
- no problems with catalyst attrition;
- larger catalyst loading of the reactor possible.

Three phase slurry reactor:

- no intra-particle diffusion limitations due to use of sufficiently small catalyst particles;
- good isothermal operation due to excellent heat transfer, both within the slurry as well as to the cooling system;

- catalyst can be added and removed during operation, leading to a larger availability of the reactor.

FT synthesis produces a distribution of linear paraffins and olefins with a wide range of molecular weights. The chain length of these hydrocarbons can vary according to the catalyst properties and operating conditions. Long chain heavy paraffins with waxy properties can be produced and need to be cracked to shorten the chain length [22]. In a typical FT product distribution, as listed in Table S2.1, it is found that nearly half of the total amount of products is heavy oils and waxes.

Upgrading heavier products is mostly carried out using catalysts, such as Pt and Pd, or bimetallic materials, such as Ni/Mo, Ni/W, and Co/Mo in their sulfided forms, supported on substrates of oxide mixtures (e.g.. aluminum oxide, etc.), zeolites or silicoaluminophosphates [22]. The catalysts are normally designed as bi-functional, promoting hydrocracking and isomerization on acidic sites and hydrogenation and dehydrogenation on metallic sites. The degrees of isomerization and hydrocracking are controlled by the catalyst system and reaction conditions. The resulting gaseous by-products from the upgrading reactors can be used to generate power in a combined cycle system.

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Supporting Information S3

Pyrolysis

Technical Description of Fast Pyrolysis Reactors:

Fluidized-bed Pyrolyzer: Bubbling and circulating fluidized-beds are two broad types of reactors used for fast-pyrolysis of biomass.

Bubbling fluidized-beds (BFB): Bubbling fluidized-beds have the benefit of well-established technology and ease of construction and operation. They are widely used in engineered chemical processes [1-3]. Heat can be provided to the reactor in a variety of ways and scaling is well understood. However, at large scale, heat transfer may become problematic (>200 Mg/d, ~40 MW_{th}) [3]. Biomass particle sizes of less than 3 mm are required to ensure a rapid heat transfer to the biomass particles and to produce an acceptable bio-oil yield (2 mm is typically used [1]). The energy content of the char is usually more than sufficient to supply the thermal requirements of the pyrolyzer and is generally used for this purpose [3]. The char separation is easier than in circulating FB reactors and can be exported if another heat source for driving the pyrolysis reactions is preferred. Due to high inert gas flow rates through this type of reactor, larger processing equipment is needed than for rotating cone or ablative process designs which increases costs and reduces the net efficiency [1] as discussed in the summary at the end of this sub-section.

The largest bubbling bed units currently operating or under construction are: 100 Mg/d and 200 Mg/d units in Canada (two pilot and two commercial) based on a design by Resource Transforms International and built by Dynamotive (Mg/d refers to dry-feedstock input). Biomass Engineering Ltd in the UK is constructing a 6 Mg/d plant. Fortum built a 12 Mg/d plant in Finland which has since been dismantled. Metso, working with UPM and VTT in Finland, constructed and operated a 55 Mg/d unit in Tampere, Finland. Anhui University of Science and Technology in China is overseeing construction of three 14 Mg/d demonstration plants in China [3].

Circulating fluidized-beds (CFB): Circulating fluidized-beds and transport reactors have many of the same elements as BFB designs described above. The main drawback compared to a BFB reactor is that char is more difficult to remove from the bio-oil. CFBs have the potential for greater throughput than BFBs and their construction and operation is well understood from petro- and petro-chemical industries [1, 3, 4]. Envergent Technologies is marketing a commercial unit of 400 Mg/d [5] compared to the largest bubbling-bed reactors which operate at 200 Mg/d [3, 6, 7]. Heat is typically supplied by recirculating hot sand from a second (inter-connected) combustion reactor, which can be a bubbling or circulating fluidized-bed. The biomass particle size required for CFB reactors is typically 2-6 mm [8]. Char is not typically recovered from CFB processes as it is usually burned in the secondary combustion reactor to sustain the pyrolysis reactions. The char could be recovered (as a fine powder) and an alternative heat source used to drive the process [3, 6, 8].

A number of circulating bed reactors are in operation. The most notable is operated by Ensyn, which has built several units in the USA and Canada. They are reported to operate at ~40 and 100 dry Mg/d [3] with one unit operating at 400 a dry Mg/d plant in Malaysia. Fifteen fast pyrolysis plants (using Ensyn's technology) were planned by 2015 under the Malaysian Premium Renewable Energy's bio-oil project [6]; however no information on the current state of this project could be identified (Aug 2016). Ensyn and UOP have a joint venture under the name Envergent Technologies to exploit this technology for bio-oil production. They are marketing 150 and 400 Mg/d commercial units [9]. An alternative CFB fast-pyrolysis process is being developed by Metso and UPM, (Finland) who operate a 10 Mg/d demonstration unit [3].

A press release in Aug. 2016 reported than Ensyn are building a fast pyrolysis facility in Port Cartier, Quebec, due for completion late 2017. The facility will convert 65,000 dry Mg of forest residues per year to ~10 million gallons of RTP green fuel (~40 million liters) [10].

Rotating cone reactors: Rotating cone reactors can be thought of as a transported bed reactor; however, centrifugal forces are used for feedstock transport instead of a carrier gas [3, 4]. A small amount of inert gas is required to transport hot sand from the combustor to the pyrolyzer. The main advantage of this design is the much reduced flow of carrier gas which makes bio-oil recovery easier and process equipment smaller when compared to FB reactors [3]. On the negative side, the required biomass particle size is smaller than for fluidized-beds, typically 0.2 mm [1]. In addition, it is more difficult to integrate the different units in this process route which makes construction more complex than for FB reactors. As with CFBs, all the char is consumed to provide the heat for the process but could be recovered if an alternative heat source were available [3, 4, 11].

Rotation cone pyrolyzers were invented at the University of Twente, the Netherlands and Biomass Technology Group (BTG, [12]) of the Netherlands developed the process. A 6 Mg/d unit is operational and a 50 Mg/d plant was installed in Malaysia in 2004 to produce bio-oil for co-firing in a stationary diesel engine [3, 6]. In early 2015 BTG completed construction of a 120 Mg/d fast pyrolysis facility in Hengelo, the Netherlands (the Empyro plant) [12]. A 120 Mg/d reactor is currently the largest commercially available unit according to the BTG website, although a 240 Mg/d unit and larger will be available in the near future (as of Aug. 2016) [12]. To date around 45 types of feedstock have been tested, including rice husk and sugarcane bagasse.

Upgrading of Fast Pyrolysis Bio-oil

Bio-oil has roughly half the heating value of petroleum derived fuel oil and is of poor quality in terms of viscosity, water content, oxygen content and energy density compared to petroleum or coal derived fuels [1, 3, 13]. For these reasons, upgrading of bio-oil is an attractive option. Upgrading is a broad term used to describe different processes which can be physical, chemical, or catalytic. In the discussion below, only catalytic and chemical (i.e. non-catalytic chemical methods) processes are referred to by the term upgrading in relation to the treatment of the bio-oil. Upgrading can be performed locally or remotely (coupled or decoupled). Coupled processes include the use of a catalyst inside the pyrolysis reactor (catalytic pyrolysis) or downstream in a dedicated reactor. Decoupled processes treat the recovered bio-oil at a remote location from its production, either in the liquid phase or by re-volatilization of the bio-oil [1, 3].

Comprehensive reviews of upgrading methods for bio-oils including detailed technical and economic information have been reported. The main conclusions reported herein are a brief summary of information from those articles.

When used as an intermediate, bio-oil is upgraded to biofuels or chemicals, which can then be refined conventionally. Upgrading is achieved catalytically or chemically. Many different approaches have been studied which can be grouped into four main areas of activity [3]:

1) Hydro-treatment (catalytic cracking)
2) Zeolite cracking (catalytic vapor cracking)
3) Other chemical upgrading methods (esterification and related processes)
4) Gasification with Fischer-Tropsch synthesis of liquid fuels and chemicals

Given all the potential options and the lack of information from commercial companies, it is not possible to identify a ‘best route’ at present. A brief account of the four main approaches is provided below.

1) Hydro-treatment

Hydro-treatment of bio-oil involves de-oxygenation through a catalytic process which results in a naptha-like product that can be refined conventionally. Current processes require high pressure (up to 20 MPa, 200 bar), medium temperature (up to 400°C) and a supply of hydrogen. This is an operation that can be performed remotely from pyrolysis; i.e. at a centralized refinery, to benefit from economies of scale and integration [1-3].

The expected yield of naptha from biomass is approximately 25 wt% of the dry starting biomass (55% in terms of energy, basis not given) if hydrogen is *not* accounted for [3]. If the hydrogen is assumed to come from biomass gasification, the yield is reduced to 15 wt% by dry weight (33% energy, basis not given) of the starting biomass [3]. Gasification for the hydrogen requirement would require an additional input of biomass equal to 80 wt% of the biomass used to produce the bio-oil, for full hydro-treatment [3].

The catalysts traditionally used for hydro-treatment are CoMo and NiMo on alumina or alumina-silicate supports [3]. More recently, precious metal catalysts have been studied on a variety of supports. Of note are catalysts being developed and tested by UOP and Pacific Northwest National Laboratory in the USA, GroningenUniversity in the Netherlands and Technical University of Munich Lercher, Germany. Other research groups are also active and comprehensive accounts of on-going studies can be found elsewhere [1-3]. The main concerns for hydro-treatment are coke and gas formation as well as catalyst deactivation and the high pressure and hydrogen requirements [1, 3].

UOP LLC is building a 1 t/d (dry-input) pilot scale unit at the Tesoro refinery in Oahu, Hawaii. From available information [5, 9, 14-16], the yield of bio-oil is projected to be ~635 L (760 kg) per dry tonne of biomass. Upgrading is planned using a two-stage hydro-treating method. However, information regarding temperature, hydrogen requirement, pressure and catalyst is propriety. It has been reported by UOP at a recent conference [5, 9] that the targeted yield from the upgrading unit is 90 gallons of diesel equivalent from one tonne dry biomass input; that is 340 L of diesel (290 kg, 0.85 kg/L, zero moisture). On this basis, the mass conversion of bio-oil to diesel equivalent fuel is 38% [9].

The approximate net fuel-based efficiency is 73% on a $LHV_{a.r}$ basis for converting one tonne of biomass with 7 wt% M.C ($LHV_{a.r}$ 17.0 MJ/kg) to 290 kg of diesel ($LHV_{a.r}$ 42.5 MJ/kg). On a HHV_{dry} basis, the $Eff_{N\text{-}FB}$ is roughly 65% for biomass with an HHV_{dry} of 19.7 MJ/kg. However, these values do *not* account for the considerable energy inputs required for upgrading. No specific information is available in this regard for the UOP process. Therefore, a net process-based efficiency cannot be determined.

The net efficiency (process-based) of a general hydro-treatment process has been estimated as 50% when considering the energy required to catalytically upgrade and refine the bio-oil into transportation fuels, and as 40% when considering the full life cycle [1] (on a HHV basis). In a separate review article, a $Eff_{N\text{-}PB}$ of 33% was reported [3] (no basis was given).

2) Zeolite cracking (catalytic vapor cracking)

Zeolite cracking rejects oxygen from the bio-oil as CO_2 and produces a hydrocarbon product that can be refined conventionally. Zeolite catalysts are often used to aromatize aliphatic compounds [1]. This operation can be integrated with the pyrolysis step or performed remotely on bio-oil or revaporized bio-oil.

Research to find more suitable catalysts and processes to generate different ranges of products (biofuels to chemicals) is ongoing. There are more than twenty different catalysts / processes under investigation [1-3]. The studies can be grouped into four main areas of activity: (a) integrated catalytic pyrolysis; (b) close coupled vapor upgrading; (c) decoupled vapor upgrading from volatilization of bio-oil; and (d) decoupled liquid bio-oil upgrading.

(a) Integrated catalytic pyrolysis can be achieved in several ways and there have been a number of developments in recent years. Anellotech is a spinoff company from a process developed by G. Huber at the University of Massachusetts Amherst. A product called grassoline is produced from biomass pyrolysis using ZSM-5 catalyst. Production of gasoline, diesel, heating oil, benzene, toluene and xylenes has been demonstrated, although yields are low [3, 17]. BioECon has a joint venture with KIOR but little information is available other than modified clays have been studied as has impregnation of biomass with nano catalysts prior to pyrolysis. Success is claimed at temperatures as low as 230°C [3]. However, it is unlikely that methods which involve impregnating biomass with a catalyst would be viable in a commercial process. KIOR went bankrupt in 2015 while attempting to commercialize their upgrading process. CPERI in Greece is using zeolites and mesoporous catalysts in circulating fluidized-bed reactors; evidence of upgrading was reported but de-oxygenation was incomplete [3]. Several other groups and commercial companies are also active [1, 3].

A drawback of operating an integrated catalytic pyrolysis system is that it limits the flexibility of the process (as a single temperature must be maintained) and the catalyst has to survive the harsh chemical and mechanical environment. Coking, gas formation and catalyst regeneration are other recognized problems [1, 3].

(b) Close coupled vapor upgrading is the catalytic cracking of vapors over acidic zeolite catalysts. The process deoxygenates bio-oil by simultaneous dehydration-decarboxylation at 450°C and produces mostly aromatics [1, 3]. The unit would operate much as a fluid catalytic cracking (FCC) unit in a petroleum refinery. A projected yield is ~20% aromatics by weight of the starting dry biomass (45% in energy terms, basis not stated). The aromatic product is suitable for blending with gasoline and can be refined conventionally. A benefit of this approach is that hydrogen is not required and it operates at atmospheric pressure [3].

Catalyst deactivation and control over products are the main concerns for both process routes described above. At present, costs are high and yields are low [1, 3].

(c) Decoupled vapor upgrading from volatilization of bio-oil and (d) decoupled liquid bio-oil upgrading involve the upgrading of bio-oils remotely from their production. These approaches benefit from being able to locate the upgrading processes at a single location such as a refinery and to operate at a larger scale to improve economics. Many of the processes are similar to those described above (integrated catalytic pyrolysis and close coupled vapor upgrading), but less effective due to the bio-oil having to be re-vaporized or treated in the liquid phase. Limited information is available regarding which of the many routes being investigated are closest to commercialization. A thorough review of these processes can be found elsewhere [1].

3) Other chemical upgrading methods (esterification and related processes):

In this sub-section, other non-physical upgrading methods are presented. More than ten additional catalysts / process routes are being actively studied [1, 3]. The most notable are summarized below.

Mild cracking occurs when only the cellulose and hemicellulose derived products of bio-oil are cracked over base catalysts with the aim of reducing coking and gas formation. Work is ongoing at the University of Kentucky exploring ZnO, Zn/Al and Mg/Al layered double hydroxides to upgrade bio-oils based on earlier work in Finland [3].

Esterification and other processes seek to improve bio-oil quality without de-oxygenation. The properties addressed by esterification are mainly water content, acidity, stability and reactivity. University of Georgia, USA, is studying esterification of pyrolysis vapors. Zhejiang University, China, is working on hydrogenation and esterification over bi-functional platinum catalysts [1, 3].

Bio-oil contains a significant amount of water (15-30% wt.) that contributes to reduced heating value and acidity. Removing this water by evaporation is not possible because the bio-oil will react, resulting in a lower value product. Alternatively, water can be added to the bio-oil to produce a phase separation at concentrations higher than ~35 wt% water. However, a use for the aqueous phase is necessary to make the process viable [3]. The aqueous phase contains mostly highly oxygenated hydrocarbons which are the most problematic for bio-oil use. Dumesic at the University of Wisconsin and Huber at University of Massachusetts Amherst are leading proponents of aqueous phase processing [1, 3, 17-20]. Aqueous reforming and dehydration / hydrogenation are used to produce hydrocarbons which can be refined conventionally. The main products from aqueous phase reforming are hydrogen and alkanes. The dehydrated bio-oil has improved properties in terms of heating value, reduced oxygen content and reduced acidity. It can be further upgraded or possibly used as a fuel oil.

4) Gasification with Fischer-Tropsch synthesis of liquid fuels and chemicals:

Bio-oil and bio-oil/char slurries can be gasified to produce a hydrogen rich gas. Steam reforming of the bio-oil or its aqueous fraction after phase separation is also being explored [3]. Interest in these process routes is mainly driven by the hydrogen requirements for hydro-treating processes described above. Nickel and other precious metal based catalysts are being studied [1-3]. Success has been achieved for the water soluble fraction of bio-oil using commercial nickel based catalysts and a process similar to natural gas reforming. However, a viable use has to be found for the organic lignin derived fraction of the bio-oil, such as a source of phenol or upgrading via different catalytic methods [3]. For example, phenol and poly-aromatic hydrocarbons can be cracked using commercial nickel-based catalysts such as G91 from SüdChemie[21] .

Summary of upgrading processes

The upgrading of bio-oil via hydro-treatment / hydro-processing has received the greatest attention in peer-reviewed literature. The process includes a low temperature hydro-treatment followed by higher temperature and high pressure hydro-cracking [4, 6, 8]. The approximate process-based net efficiency of this route is reported to be around 50%. This is higher than transportation fuels produced through biomass gasification with FT synthesis (16-43%) when compared on a common basis [1]. In a more recent review, a net efficiency of 33% was reported when the hydrogen for the hydro-treatment was provided by biomass gasification and 55% when hydrogen was not accounted for [3].

Current estimates for the volumetric yield of replacement transportation fuels that can be produced from one dry tonne of woody biomass is 340-350 L (90-92 gallons) of diesel equivalent fuel (290-300 kg) [7, 9]; i.e. ~30 % by mass.

A reoccurring conclusion from the review articles used as sources for this report was the need for further research into upgrading methods to reduce production costs and improve conversion efficiency [1-3, 22, 23].

Mass Balance of UOP LLC Circulating Fluidized Bed (CFB) process:

Through personal communication with a UOP representative [9] the following details were obtained: the mass balance for Envergent's commercial RTP units is a maximum of 65-75 wt% bio-oil, 10-20 wt% char and about 10-20 wt% fuel-gas based on the dry-feedstock. The energy content of the bio-oil is approximately 60-80% of the energy content of the biomass feedstock entering the RTP unit, based on $LHV_{a.r.}$ Using this same basis, the fuel-gas and char contain about 5-10% and 15-30% of the energy in the feedstock, respectively. The moisture contents of the biomass feedstock and the bio-oil are 4-10 wt% and 15-30 wt%, respectively. The reaction temperature is roughly 500-520°C and the hot vapour residence time is less than one second [9]. A more thorough account of the information obtained from UOP has been reported elsewhere [24].

UOP plans to upgrade RTP green fuel (bio-oil) to transportation fuels via hydro-processing at low temperature using proprietary catalysts that will require molecular hydrogen (actual temperature, pressure, and catalysts have not been made public). Output from the upgrading unit is targeted at 90 gallons of transportation fuels (340 L, 290 kg, 0.85 kg/L, $LHV_{a.r}$ 42.5 MJ/kg, based on diesel) from 1 Mg of dry biomass input to the RTP unit. If the distillate residue is also considered, the output from the upgrading unit is expected to be 100 gallons of petroleum equivalent liquid fuels[9].

Under best case scenarios, the LHV efficiencies of RTP green fuel production (based on the definitions in Supporting Information Section S4) from a 400 Mg/d unit operating with feedstock moisture of 4-10 wt% and producing RTP green fuel with a moisture content of 15-30 wt% are:

Net thermal efficiency$_{\text{fuel-basis}}$ (Eff$_{\text{N-FB}}$) $\cong$ 65-70%,

Gross thermal efficiency$_{\text{fuel-basis}}$ (Eff$_{\text{G-FB}}$) $\cong$75-80%

Net thermal efficiency$_{\text{process-basis}}$ (Eff$_{\text{N-PB}}$) $\cong$ 65-70%

Gross thermal efficiency$_{\text{process-basis}}$ (Eff$_{\text{G-PB}}$) $\cong$ 70-75%

According to UOP there is no significant difference in efficiency between the 150 Mg/d and 400 Mg/d units. Information regarding the efficiency of UOP's upgrading process, cost data for production of RTP green fuel (bio-oil) or transportation fuels, and capital and operating costs for a commercial unit are currently unavailable [9].

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Supporting Information S4

Terminology (Energy and Efficiency)

Heating values: all fuels have two heats of combustion at constant volume (also referred to as calorific or heating values):

1) Higher heating value (HHV) – heat released by complete combustion of fuel to CO_2 and H_2O products; H_2O in liquid phase (heat of condensation recovered)

2) Lower heating value (LHV) – heat released by complete combustion of fuel to CO_2 and H_2O products; H_2O in vapor phase (heat of condensation not recovered)

Both the HHV and LHV can be reported on a moist (as-received) or dry basis. The HHV is determined experimentally on the dry sample (ASTM E711-81 or D2015-77), and the HHV of the as-received sample can then be derived from the weight fraction of biomass in the a.r sample multiplied by the HHV_{dry} of the sample (Eq. D1.1) [1]:

$$HHV_{a.r} = (1-M_{wb}) * HHV_{dry} \tag{D1.1}$$

where M_{wb} is moisture content of the fuel on a wet basis (decimal).

The LHV for any moisture content can also be derived from the HHV_{dry} using equation D1.2 [1]:

$$LHV = (1-M_{wb}) \{HHV_{dry} - \lambda(M_{db} + 9H)\} \tag{D1.2}$$

where λ is the latent heat of water vaporization (2.31 MJ/kg at 25°C, constant volume), M_{wb} is moisture content of the fuel on a wet basis (decimal), M_{db} is the moisture content on a dry basis (decimal) and H is the mass fraction (decimal) of hydrogen in the fuel on a dry basis [1].

However, it is important to note that biomass pyrolysis oil (bio-oil) is a special case as moisture cannot be easily removed without changing the properties of the sample. Therefore, the HHV is determined experimentally on the a.r sample (with moisture present, $HHV_{a.r}$) [1, 2]. This can lead to confusion as the LHV and HHV for bio-oil are often reported without the basis stated (dry or a.r) which makes comparing information from different authors and processes difficult. In addition, even if the basis of the heating value is stated, if the moisture and hydrogen contents are not provided, it is not possible to normalize data sets to an equivalent basis which further hinders comparisons.

Note regarding efficiencies: When discussing the efficiencies of thermal processes (in general) the terms 'process thermal efficiency' (PTE) or 'thermal efficiency' are often used interchangeable but are rarely defined in literature. One definition was found for PTE; "the PTE is defined as the percentage of energy in the products divided by the energy in the biomass feedstock [3]". Elsewhere 'thermal efficiency' has been defined in the same manner on an $LHV_{a.r}$ basis [4]. These definitions do not account for the energy required to produce the product.

The term 'net efficiency' or 'net energy efficiency' has been defined as the energy in the products divided by the energy in the biomass feedstock, after accounting for the energy required to produce the product (drying, sizing, pyrolyzer and recovery, including thermal and electrical energy) using $LHV_{a.r}$ [4] and elsewhere on a HHV basis [3]. These were the only cases found where the net efficiency was defined or reported for a fast-pyrolysis process.

In regard to the pyrolysis platform the following terms defined below will be used when discussing efficiencies (equations D1.3 to D1.6). In cases where the basis of the efficiency was not given in the cited literature source it will be indicated in the text.

Net thermal efficiency$_{\text{fuel-basis}}$ ($\text{Eff}_{\text{N-FB}}$)

$$= \text{energy in bio-oil} / \text{energy in biomass} \qquad \text{(D1.3)}$$

Gross thermal efficiency$_{\text{fuel-basis}}$ ($\text{Eff}_{\text{G-FB}}$)

$$= (\text{energy in bio-oil} + \text{useful energy products}) / \text{energy in biomass} \qquad \text{(D1.4)}$$

Net thermal efficiency$_{\text{process-basis}}$ ($\text{Eff}_{\text{N-PB}}$)

$$= \text{energy in bio-oil} / (\text{energy in biomass} + \text{auxiliary energy input}) \qquad \text{(D1.5)}$$

Gross thermal efficiency$_{\text{process-basis}}$ ($\text{Eff}_{\text{G-PB}}$)

$$= (\text{energy in bio-oil} + \text{useful energy products}) / (\text{energy in biomass} + \text{auxiliary energy input}) \qquad \text{(D1.6)}$$

where, ‘useful energy products’ = fuel-gas, char, process heat or electricity.

Note regarding energy balances: Detailed information regarding energy balances for most thermochemical and biochemical processes are often proprietary. Energy balances for fast pyrolysis processes are typically reported as follows, ‘the bio-oil contains 70-75% of the energy in the starting biomass, the char 20-25% and the fuel-gas 5-15% [5-7]. However, it is rarely stated if this is derived from LHV or HHV, as-received or dry materials, or if supplemental energy requirements are accounted for. On the few occasions when a basis is given, it is often still not possible to convert the data to a common basis as other information is lacking, (e.g. moisture and hydrogen contents of the feedstock and products). These inconsistencies in the literature and information reported by technology developers make detailed comparisons of efficiencies between different reactor types or processes difficult. The difference between the net and gross efficiencies (also fuel-based or process-based) can be relatively minor for fast-pyrolysis processes if the only product is bio-oil and all the char and fuel-gas are used to provide the thermal requirements of the plant with a relatively small supplemental electrical requirement. However, this is not always the case, as the char and fuel-gas utilization and supplemental energy requirements vary (discussed further elsewhere [8]).

In light of these issues, individual mass and energy balances cannot be justified for each type of fast-pyrolysis reactor that is currently available (further information on different designs of fast pyrolysis reactor can be found elsewhere [7, 8]). Instead, the following generic efficiencies are considered a reasonable estimate for all the fast-pyrolysis systems discussed herein:

Net thermal efficiency$_{\text{fuel-basis}}$ ≈ 65% based on LHV$_{\text{a.r}}$ where the moisture content (M.C.) of the starting biomass is 6-10 wt% and the bio-oil M.C. is 15-25 wt%. Based on HHV$_{\text{dry}}$, the Eff$_{\text{N-FB}}$ is approximately 75%.

Net thermal efficiency$_{\text{process-basis}}$ ≈ 60% on a LHV$_{\text{a.r}}$ basis (same M.C. as above) and 70% on a HHV$_{\text{dry}}$ basis.

In both cases only the pyrolysis oil (bio-oil) was considered as an exportable product and heat losses were not accounted for. All the char and fuel-gases are consumed to provide local heat requirements. Therefore, by using these assumptions, the net and gross efficiencies are identical.

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