

Bio-Jet Fuel Conversion Technologies

Wei-Cheng Wang^{1*} and Ling Tao²

1. Department of Aeronautics and Astronautics, National Cheng Kung University, No.1, University Road, Tainan, Taiwan 70101
2. National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401

*Corresponding author

Abstract

Biomass-derived jet (bio-jet) fuel has become a key element in the aviation industry's strategy to reduce operating costs and environmental impacts. Researchers from the oil-refining industry, the aviation industry, government, biofuel companies, agricultural organizations, and academia are working toward developing a commercially viable and sustainable process that produces a long-lasting renewable jet fuel with low production costs and low greenhouse emissions. This jet fuel, additionally, must meet ASTM International specifications and potentially be a 100% drop-in replacement for current petroleum jet fuel. In this study, the current technologies for producing renewable jet fuels, categorized by alcohols-to-jet, oil-to-jet, syngas-to-jet, and sugar-to-jet pathways are reviewed. The main challenges for each technology pathway, including conceptual process design, process economics and life-cycle assessment of greenhouse gas emissions are discussed. Although the feedstock price and availability and energy intensity of the process are significant barriers, biomass-derived jet fuel has the potential to replace a significant portion of conventional jet fuel required to meet commercial and military demand.

Key words: Bio-jet fuel; alcohol-to-jet; hydro-processed renewable jet; Fischer-Tropsch; catalytic upgrading sugars to hydrocarbons; direct sugar to hydrocarbon

Author contact information:

Wei-Cheng Wang
Tel: +886-6-2757575 ext. 63628
Email: wilsonwang@mail.ncku.edu.tw <mailto:wwang77777@gmail.com>

Acronyms

ABE	acetone-butanol-ethanol
AFRL	U.S. Air Force Research Laboratory
APR	aqueous phase reforming
ASTM	ASTM International
ATJ	alcohol-to-jet
BIRD	Binational Industrial Research and Development
BTL	biomass-to-liquid
CH	catalytic hydrothermolysis
CLEEN	Continuous Lower Energy, Emissions and Noise
CO	carbon monoxide
CO ₂	carbon dioxide
CTL	coal-to-liquid
DARPA	Defense Advanced Research Projects Agency
DCN	Derived Cetane Number
DMF	2,5-dimethylfuran
DOE	U.S. Department of Energy
DSH	Direct Sugar to Hydrocarbons
<i>E. coli</i>	<i>Escherichia coli</i>
FAA	Federal Aviation Administration
FFA	free fatty acid
F-T	Fischer-Tropsch
gCO ₂ e	grams carbon dioxide equivalent
GGE	gallon of gasoline equivalent
GHG	greenhouse gas
GJ	gigajoules
GTJ	gas-to-jet
GTL	gas-to-liquid
H ₂	hydrogen
HDCJ	hydrotreated depolymerized cellulosic jet
HEFA	hydroprocessed esters and fatty acids
HMF	5-hydroxymethylfurfural
HRJ	hydroprocessed renewable jet
LCA	life-cycle assessment
LHV	lower heating value
MIL	military
MJ	megajoules
NAWCWD	Naval Air Warfare Center Weapons Division
NO _x	oxides of nitrogen
NETL	National Energy Technology Laboratory
NRC	National Research Council Canada
NREL	National Renewable Energy Laboratory
OTJ	oil-to-jet
READI	renewable, aromatic, and drop-in
RTP	rapid thermal processing
SPK	synthetic paraffinic kerosene
STJ	sugar-to-jet
TTW	tank-to-wake
WTT	well-to-tank
WTW	well-to-wake

Table of Contents

1	Introduction.....	4
	1.1 Background	4
	1.2 Jet Fuel Specifications	5
	1.3 Bio-Derived Jet Fuel Conversion Pathways	7
2	Conversion Pathways to Bio-jet Fuel.....	9
	2.1 Alcohol-to-Jet (ATJ) Fuel	9
	2.1.1 Process Description.....	9
	2.1.2 Economic Analysis	11
	2.1.3 Life-Cycle Assessment	12
	2.2 Oil-to-Jet (OTJ) Fuel	12
	2.2.1 Process Description.....	12
	2.2.1.1 Hydroprocessed Renewable Jet (HRJ).....	12
	2.2.1.2 Catalytic Hydrothermolysis (CH).....	14
	2.2.1.3 Hydro-treated Depolymerized Cellulosic Jet (fast pyrolysis with upgrading to jet fuel)	15
	2.2.2 Economic Analysis	15
	2.2.3 Life-Cycle Assessment	17
	2.3 Gas-to-Jet (GTJ) Fuel	17
	2.3.1 Process Description.....	18
	2.3.1.1 Fisher Tropsch Biomass to Liquid (FT-BTL) Process.....	18
	2.3.1.2 Gas Fermentation Process.....	19
	2.3.2 Economic Analysis	20
	2.3.3 Life-Cycle Assessment	20
	2.4 Sugar-to-Jet Fuel	21
	2.4.1 Process Description.....	21
	2.4.1.1 Catalytic Upgrading of Sugars to Hydrocarbons	21
	2.4.1.2 Direct Sugar to Hydrocarbons (DSH).....	23
	2.4.2 Economic Analysis	24
	2.4.3 Life-Cycle Assessment	24
3	Summary of all bio-jet fuel production pathways.....	25
4	Conclusion	31
	Acknowledgement	31
	Reference	31

1 Introduction

1.1 Background

Fuel is one of the biggest operating costs for the aviation industry. Aviation fuel, a petroleum-based fuel used to power aircraft, has stricter quality requirements than fuels used in road transport. Jet fuel, a type of aviation fuel designed specifically to power the gas-turbine engines, will be the primary subject of this review. According to a report from the U.S. Department of Energy's (DOE's) Bioenergy Technologies Office [1], out of one barrel of crude oil, 4 gallons are used to produce jet fuel. The worldwide aviation industry consumes approximately 1.5 to 1.7 billion barrels (47.25 to 53.55 billion gallons) of conventional jet fuel per year [2, 3]. The challenges of crude oil prices, national security, environmental impact, and sustainability make it difficult to have a long term plan and budget for operating expenses. Sustainable biofuels produced globally offer a solution to these issues. Biomass-derived jet fuels (bio-jet fuels) are a potential alternative to petroleum jet fuel.

Many process technologies that convert biomass-based materials into jet fuel substitutes are available. Some are available at commercial or pre-commercial scale, and others are still in the research and development stage. These technologies are varied and depend strongly on the type of feedstock. Oil-based feedstocks are converted into bio-jet fuels through hydro-processing technologies, including hydro-treating, deoxygenation, and isomerization/hydrocracking. Processes such as catalytic hydro-thermolysis (CH) have also been developed to treat triglyceride-based oils. Solid-based feedstocks are converted into biomass derived intermediate through gasification, into alcohols through biochemical or thermochemical processes, into sugars through biochemical processes, and into bio-oils through pyrolysis processes. Syngas, alcohols, sugars, and bio-oils can be further upgraded to bio-jet fuel via a variety of synthesis, fermentative, or catalytic processes. So far, bio-jet fuels from Fischer-Tropsch (F-T) synthesis and oil hydro-processing technologies have been approved by ASTM International (ASTM) Method D7566 [4] for blending into jet at levels up to 50%. Hydro-processing technologies using vegetable and waste oils represent the only conversion pathways ready for large-scale deployment [5]. Industries are currently working on developing optimal processes that utilize sustainable feedstocks and can be produced economically.

Production cost is a key parameter of the commercial feasibility of a bio-jet fuel. U.S. passenger and cargo airlines require more than 18 billion gallons of jet fuel annually. Therefore, every penny increase in the price of jet fuel results in an additional \$180 million in annual fuel costs for U.S. airlines [6]. The price of petroleum-derived jet fuel is directly correlated with the price of crude oil [7]. Changes in crude oil price make it difficult to plan and budget long-term operating expenses for jet fuel refining. In 2012, the annual fuel cost for all airlines was around \$47 billion [8]. It is predicted that by 2030, the bio-jet fuel production cost may drop to as low as \$2.54/gal due to improved conversion technology [9], and 30% of annual airline fuel consumption can be replaced by bio-jet fuel [2]. Following the same pattern for bioethanol production [10], the variation in the bio-jet production cost would be highly dependent on the following parameters: (1) composition and cost of feedstock; (2) process design; (3) conversion efficiency or product yield; (4) valorization of co-products; and (5) energy conservation. Therefore, decreasing the production cost of bio-jet fuel depends on synergistic efforts in all areas, including improvements in the areas of feedstock productivity, extraction yield of oil or sugar yield from the crops, process energy conservation, and balance between jet fuel product and value-added co-products.

In addition, there is a growing awareness of important environmental issues, including improving air quality in and around airports and determining the aviation industry's contribution to greenhouse gas (GHG) emissions globally. It has been estimated that commercial aviation has contributed approximately 2%–6% to total global carbon emissions [11]. Jet fuels derived from renewable resources may offer the potential to reduce the GHG emissions from aviation. A life-cycle assessment (LCA) that considers emissions from the field where the feedstock is harvested to the wake behind the aircraft can provide the change in GHG emissions due to the use of alternative fuels [3], usually known as well-to-wake (WTW) analysis. The WTW analysis can be split into two parts: well-to-tank (WTT) and tank-to-wake (TTW)

[12]. To compare the GHG emissions due to bio-jet fuels with that of conventional jet fuels, it is necessary to consider emissions from the whole production chain. In the WTT portion, feedstock production, land use change, and conversion processes contribute significantly to GHG emissions. In the TTW portion, emissions from burning jet fuels are considered [12]. The WTW GHG emissions from conventional jet fuel are reported to be 87.5 grams carbon dioxide equivalent per megajoule ($\text{gCO}_2\text{e}/\text{MJ}$) [13], including 14.3 $\text{gCO}_2\text{e}/\text{MJ}$ WTT GHG emissions and 73.2 $\text{gCO}_2\text{e}/\text{MJ}$ TTW GHG emissions [14]. When bio-jet fuel is used for aviation, the GHG emissions can be reduced to 1.5 $\text{gCO}_2\text{e}/\text{MJ}$ (open pond algal oil case), a 98% reduction relative to conventional jet fuel [15]. Different conversion technologies may result in different amounts and types of GHG emissions due to the variety of feedstocks and reaction processes. Reviewing the GHG emissions data from the conversion pathways will help determine the optimal platforms for producing bio-jet fuel.

Groups such as aircraft manufacturers, airline companies, academic institutions, fuel refining companies, agricultural companies, farmers groups, and local/regional/national departments of agriculture, defense, transport, economic development, and enterprise are working together to develop commercially feasible bio-jet fuel [16]. The level of bio-jet fuel commercialization depends on feedstock availability, conversion technology development, reduction of GHG emissions, and policy. Conversion technologies for transportation biofuels such as ethanol [17] and biodiesel [18] have been reviewed and compared extensively. For future development and deployment of bio-jet fuel, it is important to review and understand the maturity and uncertainty of all pathways to assess impacts on commercialization.

1.2 Jet Fuel Specifications

In addition to define target compositions, jet fuel specifications and requirements are mostly defined in terms of required performance properties. The specifications required for jet fuels are (1) acceptable minimum energy density by mass, (2) maximum allowable freeze point temperature, (3) maximum allowable deposits in standard heating tests, (4) maximum allowable viscosity, (5) maximum allowable sulfur and aromatics content, (6) maximum allowable amount of wear in standardized test, (7) maximum acidity and mercaptan concentration, (8) minimum aromatics content, (9) minimum fuel electrical conductivity, and (10) minimum allowable flash point [19]. There are three standards for certifying aviation fuel : ASTM D1655 [20, 21], International Air Transport Association Guidance Material (Kerosene Type) [20, 21], and the United Kingdom Ministry of Defence, Defence Standard (Def Stan) 91-91 [22]. ASTM Specification D7566 (Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons), which targets alternative jet fuel, lists the fuel properties and criteria required to control the production and quality of a renewable fuel for aviation safety [23]. There might be other fuel standards, and Table 1 shows the specifications for two typical jet fuels for commercial and military aircraft. Jet fuel requires a high flash point due to the fire-hazard consideration [24]. Major fuel properties are similar across different standards, but there are some differences. For instance, D7566 is an expansion of D1655 to include fuel specifications required of the SPK blendstocks. In addition, jet fuel needs good cold flow properties, such as a lower freezing point, to ensure the fuel can flow at high altitude [25].

Table 1. Jet Fuel Specifications [19, 22-24, 26]

	Jet A-1				JP-8
	ASTM D1655-04a	IATA	Def Stan 91-91	ASTM D7566	MIL-DTL-83133E specification
Composition					
Acidity, Total (mg KOH/g)	0.1, max	0.015, max	0.012, max	0.1, max	0.015, max
Aromatics (vol %)	25, max	25, max	25, max	25, max (8, min)	25, max
Sulphur, Total (wt %)	0.3, max	0.3, max	0.3, max	0.3, max	0.3, max
Volatility					
Distillation Temperature:					
10% Recovery (°C)	205, max	205, max	205, max	205, max	205, max
20% Recovery (°C)	---	---	---	---	---
50% Recovery (°C)	---	---	---	--- (15, min)	---
90% Recovery (°C)	---	---	---	---(40, min)	---
Final BP (°C)	300, max	300, max	300, max	300, max	300, max
Flash Point (°C)	38, min	38, min	38, min	38, min	38, min
Density @ 15°C (kg/m ³)	775-840	775-840	775-840	775-840	775-840
Fluidity					
Freezing Point (°C), max	-47	-47	-47	-40 Jet A ; -47 Jet A-1	-47
Viscosity @ -20°C (cSt)	8, max	8, max	8, max	8, max	8, max
Combustion					
Net Heat of Comb. (MJ/kg)	42.8, min	42.8, min	42.8, min	42.8, min	42.8, min
Smoke Point (mm)	25, min	25, min	25, min	25, min	25, min
Smoke Point (mm) and Naphthalenes (vol%)	19 (min), 3 (max)	19 (min), 3 (max)	19 (min), 3 (max)	18 (min), 3 (max)	19 (min), 3 (max)
Thermal Stability					
JFTOT Delta P @ 260 °C (mm Hg)	25, max	25, max	25, max	25, max	25, max
Tube Deposit Rating (Visual)	<3	<3	<3	<3	<3
Conductivity					
Conductivity (pS/m)	50-450	50-450	50-600	---	---
Lubricity					
BOCLE Wear Scar Diameter (mm)	---	0.85, max	0.85, max	0.85, max	---

(Note: MIL-DTL-83133E is the standard specifically for JP-8 fuel)

1.3 Bio-Derived Jet Fuel Conversion Pathways

Biomass-derived jet fuel can provide a near-term and even long-term solution to the airline industry and the military with a lower environmental impact than petroleum fuels. Many bio-jet fuel conversion technologies, whether in the research and development, demonstration, or commercial stages, are described in the literature. Jet fuel blended with up to 50% bio-jet fuel from an F-T process was certified in August 2009 [12, 27-29]. Bio-jet fuels from hydro-processing technologies, such as hydro-treated esters and fatty acids (HEFA) or hydro-processed renewable jet (HRJ), were also studied extensively [30-33]. Conversion of alcohol to jet fuel, called alcohol-to-jet (ATJ), has also been developed at commercial scale and was flight-tested by the U.S. Air Force in July 2012 [34-38]. Fuel produced by two recently proposed sugar-to-jet (STJ) fuel processes, fermentation of sugars to hydrocarbons [39] and catalytic conversion of sugars to fuels [40], have been developed in joint ventures by biofuel and oil companies [41-48]. Two recently proposed processes, CH and hydro-treated depolymerized cellulosic jet (HDCJ), also called pyrolysis, have not yet been approved by ASTM, but several companies and research institutes are working on this technology [49-52]. Currently bio-jet fuels from ATJ, HRJ, and F-T synthesis have been used for commercial and military flights, as shown in Table 2.

Some of the technologies that convert bio-based feedstocks to jet fuel have been reviewed in the literature in areas including feedstock availability, upgrading technology, process economics, lifecycle GHG analysis, and commercial progress [5, 11, 12, 21, 53-57]. Most literature has focused on approved technologies such as F-T synthesis and HRJ processes; few literature references are available for either ATJ or STJ processes because they are still in the development stage. To fully understand current biomass-to-jet fuel development, it is necessary to have an overview of all of the upgrading technologies, both approved and pending approval, from laboratory to commercial scale. In this review, the upgrading pathways are classified as one of four types, based on the feedstocks and conversion processes: (1) alcohol-to-jet (ATJ), (2) oil-to-jet (OTJ), (3) gas-to-jet (GTJ), and (4) sugar-to-jet (STJ) (shown in Table 3). Detailed information and literature data, such as potential feedstocks, process technologies, cost analysis comparisons, life-cycle assessment studies, and pre-commercial or commercial demonstrations for each pathway, are described in this report in the following sections.

Table 2a. Flight Tests with Bio-jet Fuels Through Different Conversion Pathways [58] by Commercial Airlines.

Commercial Airline	Aircraft	Partners	Year	Feedstocks	Bio-jet Fuel Content	Conversion Pathway
Virgin Atlantic	B747-400	Boeing, GE Aviation	2008	Coconut & Babassu	20%	Oil to Jet
Air New Zealand	B747-400	Boeing Ralls-Royce, UOP	2008	Jatropha	50%	Oil to Jet
Continental Airlines	B737-800	Boeing, GE Aviation, CFM, Honeywell UOP	2009	2.5% Algae & 47.5% Jatropha	50%	Oil to Jet
JAL	B747-400	Boeing, Pratt & Whitney, Honeywell UOP, Nikki Universal	2009	42% Camelina, 8% Jatropha/Algae	50%	Oil to Jet
KLM	B747-400	GE, Honeywell UOP	2009	Camelina	50%	Oil to Jet
KLM	B737-800		2011	Waste cooking oil	50%	Oil to Jet
TAM Airlines	A-320	Airbus, CFM	2010	Jatropha	50%	Oil to Jet
Jet Blue Airways	A-320	Airbus, IAE, Honeywell UOP	2010	TBC		Oil to Jet
Boeing Interjet	B747-8F		2011	Camelina	15%	Oil to Jet
	A-320	CFM, Safran, EADS, Airbus, Honeywell UOP	2011	Jatropha, Halophyte	30%	Oil to Jet
Air France	A-321		2011	Waste cooking oil	50%	Oil to Jet
Honeywell	Gulfstream G450		2011	Camelina	50%	Oil to Jet
Finnair	A-319		2011	Waste cooking oil	50%	Oil to Jet
Air Mexico	B777-200		2011	Jatropha		Oil to Jet
Thomson Airways	B757-200	SkyNRG	2011	Waste cooking oil		Oil to Jet
Porter Airlines	Bombardier Q400		2012	Camelina		Oil to Jet
Air China	B747-400	Boeing, PetroChina	2012	Jatropha	50%	Oil to Jet
NRC Canada	Falcon 20, T-33	Aemetis, AFRL, Rolls-Royce, FAA-CLEEN, Agrisoma Biosciences, Applied Research Assoc., Chevron Lummus Global	2012	Carinata	100%	Oil to Jet (CH)

Lufthansa	A-321	Neste Oil	2011	Jatropha, camelina & animal fats	50%	Oil to Jet
Azul Airlines	E195 Jet	Amyris, Embraer, GE	2012	Sugarcane		Sugar to Jet
Continental Airlines	B737-800	Solazyme, United Airlines	2011	Algae		Alcohol to Jet
Alaska Airlines	B737, Bombardier Q400	Dynamic Fuels, Horizon Air	2011	Algae & waste cooking oil	20%	Oil to Jet
Virgin Atlantic		Lanza Tech, Swedish Biofuels	2011	Industrial waste gas		Gas to Jet (gas fermentation)
Etihad Airways	B777-300ER		2012	vegetable oil		Oil to Jet
British Airways	TBD	Solena	TBD	Factory waste	TBD	Gas to Jet (F-T)
Paramus Flying Club	Cessna 182		2013	Waste cooking oil	50%	Oil to Jet

Table 2b. Flight Tests with Bio-jet Fuels Through Different Conversion Pathways [58] by Military Aircrafts Types.

Military Aircraft	Aircraft	Partners	Year	Feedstocks	Bio-jet Fuel Content	Conversion Pathway
U.S. Navy	F/A-18	Honeywell UOP	2010	Camelina	50%	Oil to Jet
U.S. Air Force	A-10C	Honeywell UOP	2010	Camelina, waste cooking oil	50%	Oil to Jet
U.S. Air Force	F-22	Honeywell UOP	2011	Camelina	50%	Oil to Jet
U.S. Navy	MH60S Seahawk Helicopter		2010	Camelina	50%	Oil to Jet
U.S. Navy	MH60S Seahawk Helicopter	Solazyme	2011	Algae	50%	Oil to Jet
U.S. Navy	T-45		2011	Camelina	50%	Oil to Jet
U.S. Navy	AV-8D		2011	Camelina		Oil to Jet
Netherland Air Force	AH-64D Apache Helicopter	Honeywell UOP	2010	Waste cooking oil	50%	Oil to Jet
U.S. Air Force	A-10C	Gevo	2012	cellulose-derived alcohol		Alcohol to Jet
U.S. Air Force	B-52	Syntroleum	2006	natural gas	50%	Gas to Jet (F-T)
U.S. Air Force	TBD	Swedish Biofuels	TBD	Biomass-derived sugar	100%	Alcohol to Jet
NASA	DC-8		2011	Chicken and beef tallow		Oil to Jet
Dutch Military	Ah-64 Apache helicopter		2010	Waste cooking oil		Oil to Jet
EADs	Diamond D42		2010	Algae		Oil to Jet

Table 3. Summary of Jet Fuel Production Pathways Reviewed in This Work

Category	Pathways	Companies	U.S. or International Agencies	Airline Companies/Manufacturers
Alcohol to Jet	Ethanol to Jet	Terrabon/MixAlco; Lanza Tech/Swedish Biofuels ; Coskata	Defense Advanced Research Projects Agency, FAA	Boeing, Virgin Atlantic
	Butanol to Jet	Gevo; Byogy; Albemarle/Colbalt; Solazyme	Navy/NAWCWD, AFRL, DLA, USAF	Continental Airlines ; United Airlines
Oil-to-Jet	Hydro-processed Renewable Jet (HRJ)	UOP; SG Biofuels; AltAir Fuels; Agrisoma Biosciences; Neste Oil; PetroChina; Sapphire Energy, Syntroleum/Tyson Food; PEMEX ; ASA	U.S. Navy, USAF, Netherland Air Force, NASA, Dutch Military, EADs	Boeing, Lufthansa, Virgin Atlantic, Virgin Blue, GE Aviation, Air New Zealand, Rolls-Royce, Continental , CFM, JAL, Airbus, KLM, Interjet, Pratt & Whitney, Air China, TAM Airlines, Jet Blue Airways, IAE, United Airlines, Air France, Finnair, Air Mexico, Thomson Airways, Porter Airlines, Alaska Airlines, Horizon Air, Etihad Airways, Romanian Air, Bombardier
	Catalytic Hydro-thermolysis (CH)	Applied Research Assoc., Aemetis/Chevron Lummus Global	FAA CLEEN, NRC Canada, AFRL	Rolls-Royce, Pratt & Whitney
	Hydro-treated Depolymerized Cellulosic Jet (Pyrolysis)	Kior/Hunt Refining/Petrotech, Envergent, GTI, Dynamotive	FAA	N/A

	(HDCJ)			
Gas to Jet	Fischer-Tropsch Synthesis	Syntroleum; SynFuels; Rentech; Shell; Solena	U.S. DOE, U.S. DOD, USAF, Ontario government	Qatar Airways, United Airlines, Airbus, British Airways
	Gas Fermentation	Coskata; IneosBio/Lanza Tech; Swedish Biofuels	N/A	Virgin Atlantic
Sugar to Jet	Catalytic Upgrading of Sugar to Jet	Virent/Shell, Virdia	AFRL, U.S. DOE	N/A
	Direct Sugar to Hydrocarbons	Amyris/Total, Solazyme, LS9	Navy, FAA	Boeing; Embraer; Azul Airlines; GE; Trip Airlines

2 Conversion Pathways to Bio-jet Fuel

2.1 Alcohol-to-Jet (ATJ) Fuel

ATJ fuel, also called alcohol oligomerization, is fuel converted from alcohols, such as methanol, ethanol, butanol, and long-chain fatty alcohols. The maximum use of ethanol is 10-15% for the majority of gasoline-powered vehicles on the road today, which creates a blend wall that makes it difficult to achieve further market penetration of ethanol as a blend stock for gasoline. Therefore, upgrading ethanol to jet fuel blend stock presents a potential pathway for developing drop-in or fungible fuels for the jet fuel market. In this review, ethanol and butanol are the two primary alcohols discussed for jet fuel conversion.

2.1.1 Process Description

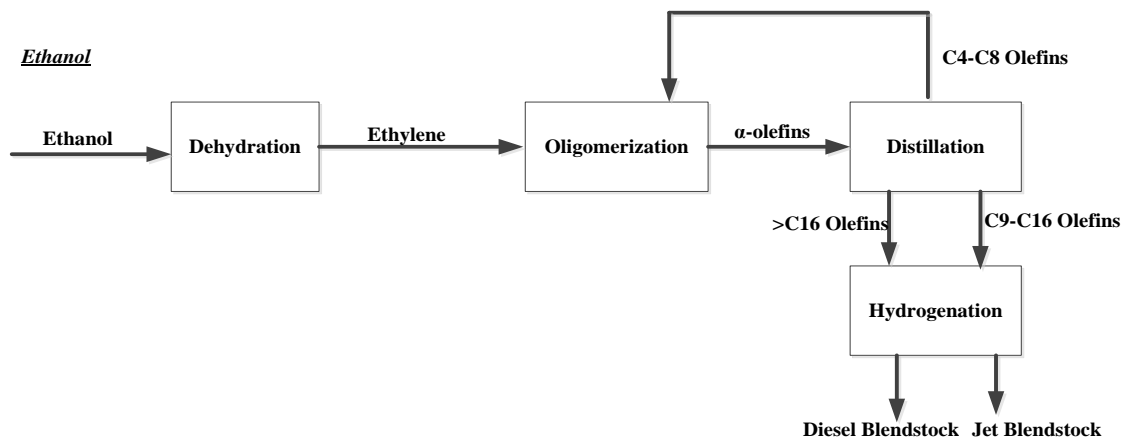
To make drop-in alternative jet fuel from alcohols, the differences in the physical and chemical properties between alcohols and conventional jet fuel have to be minimized. In the United States, anhydrous ethanol, at 99.5%–99.9% purity, is required to blend with gasoline to avoid separation [59]. However, for upgrading to jet fuel products, the necessity of high-purity ethanol is still uncertain. A typical three-step ATJ process that converts alcohols to jet fuel has been demonstrated [35]. The process includes alcohol dehydration, oligomerization, and hydrogenation. The overall process diagram for ethanol to jet fuel is shown in Figure 1. The advantage is that all of these process steps have been demonstrated on a commercially relevant scale and the risk of scale-up is expected to be reduced. However, the development and demonstration of the integrated process on biomass derived intermediates is necessary. [35].

Catalysts for upgrading alcohols to hydrocarbons are important. Studies on dehydration catalysis started with alumina and transition metal oxides and moved to silicoaluminophosphates (SAPO), H-ZSM-5 zeolite catalyst, and heteropolyacid catalysts [60]. The most promising case was found to be the 0.5% La-2%P H-ZSM-5 catalyst. Approximately 100% conversion and 99.9% ethylene selectivity are approached at 250°C and 2 h⁻¹ weight hourly space velocity [61, 62]. The dehydrated ethylene can be turned into linear α -olefins via a catalytic oligomerization process [63]. Current commercial processes for making α -olefins are focused on both homogeneous and heterogeneous catalysts [35]. Catalysts such as a Ziegler Natta-type catalyst [64], chromium diphosphine catalyst [65], and zeolites [35] have been studied extensively. With a temperature of 90°C–110°C and a pressure of 89 bar over a Ziegler Natta-type catalyst, 96%–97% yield of linear α -olefins was produced with a carbon range of C₄–C₂₀ [64]. In industrial oligomerization processes, broader carbon number distributions are produced, such as 5% C₄; 50% C₆–C₁₀; 30% C₁₂ and C₁₄; 12% C₁₆ and C₁₈; and 3% C₂₀ and C₂₀₊ [63], at 200°C and 250 bar. The resulting olefins are distilled to diesel- and jet-range fuels and light olefins [66]. Light olefins (C₄–C₈) separated by distillation are recycled back to the oligomerization step, shown in Figure 1a. Jet fuel range products (C₉–C₁₆) can be subjected to hydrogenation, which operates at temperatures of 370°C and WHSV of 3 h⁻¹ with feeding hydrogen over 5% by weight of palladium or platinum on activated carbon catalyst [67]. The C₉–C₁₆ alkanes produced from the hydrogenation step are suitable for renewable jet fuels.

N-butanol can be dehydrated to 1-butene at 380°C and 2.1 bar over the γ -alumina catalyst [68]. The highest yield of biobutenes is 98%, with 95% selectivity of 1-butene [68]. The rest of the product is 2-butene isomerized from 1-butene. The 1-butene is subjected to the oligomerization process to produce olefins ranging from C₈ to C₃₂ with the conversion of 97% [69]. The product distributions of the mixed olefins are 26.46% C₈, 25.48% C₁₂, 17.64% C₁₆, 11.76% C₂₀, 7.84% C₂₄, 4.9% C₂₈ and 3.92% C₃₂ [38].

The reaction is operated at ambient temperature with stirring for 16 hours over the Group 4 transition-metal catalysts in the presence of methylaluminoxane ($\text{Cp}_2\text{ZrCl}_2/\text{MAO}$) [70]. The 2-butene, containing cis- and trans-2-butenes, are considered as unreacted olefins and separated by temperature controlled distillation[71]. The C_8 olefin, 2-ethyl-1-hexene, is distilled and sent to the dimerization reactor [69, 72]. The dimerization is operated at 116°C for 2 hours over Nafion catalyst. The C_8 olefin is 100% converted, yielding to 90% of $\text{C}_{16}\text{H}_{32}$ [72]. The products from 1-butene oligomerization, ranging from C_{12} to C_{32} , together with C_{16} olefins produced from dimerization, are sent to hydrogenation process [72] over 0.08 wt% PtO₂ catalyst. The resulting C_{12} - C_{16} paraffins can be blended with jet fuel and the C_{20} - C_{32} alkanes are separated and sold as lubricants [69]. In addition, n-butanol from ABE fermentation can be dehydrogenated over a Pd/C- K_3PO_4 catalyst, producing C_5 - C_{11} ketones [73]. These ketones can be deoxygenated to produce normal paraffins, similar to the components of jet, gasoline, and diesel fuels. Iso-butanol produced from a process such as *E. coli* fermentation is dehydrated to a mixture of isobutene, n-butene (1-butene), and 2-butene (cis-2-butene and trans-2-butene) [74]. Acidic catalyst such as ZSM-5 zeolites, Y-type zeolites, and Amberlyst acidic resins can be used to catalyze a dehydration reaction, and different catalysts affect the selectivity of isobutene and the overall¹ linear butenes[74]. With the overall isobutanol dehydration yield of 99.1%, the selectivity is reported to be 95.1% isobutene, 1.6% 1-butene, 0.5% trans-2-butene, and 1.9% cis-2-butene at 325°C using ZSM-5 catalyst at 2 h^{-1} WHSV [74]. In addition, Armstrong reports that isobutanol can be converted into isobutylene through the dehydration process operated at 310°C over γ -Alumina catalyst, resulting in 98% isobutanol conversion and 92 mole% isobutylene selectivity [75]. The isobutene can be converted to oligomers, trimmers, and tetramers at 100°C using an Amberlyst-35 catalyst at a WHSV of 2 h^{-1} , producing 20%, 70%, and 10% for C_8 , C_{12} , and C_{16} olefins, respectively [66, 67]. The 1-butene is converted into 25%, 24%, 17%, and 25% to C_8 , C_{12} , C_{16} , and C_{20} olefins, respectively, resulting in an overall 1-butene yield of 96% with 4% unreacted. To increase the jet and diesel yields, the C_8 olefins can be distilled and sent to one additional dimerization process, operating at 116°C over a Nafion catalyst [72]. Alternatively, C_8 olefins can be either converted into $\text{C}_{16}\text{H}_{32}$ through dimerization or reacted with butenes to produce C_{12} olefins, leading to the increase of C_{12} and C_{16} for the jet-range chemicals [66].

Another source for producing 1-butene reported by researchers at the University of Wisconsin–Madison is γ -valerolactone [76]. The γ -valerolactone produced from biomass-derived carbohydrates is converted into 96% butene and CO_2 through the decarboxylation process over a silica/alumina catalyst at a pressure of 36 bar and temperature of 375°C . The resulting butene is subsequently oligomerized over an Amberlyst-70 catalyst at 170°C and 17 bar, resulting in 99% conversion of butene and 71% yield of C_8 - C_{16} alkenes, which can be targeted for jet fuel application.



¹ Unless specified, all selectivities are mass %.

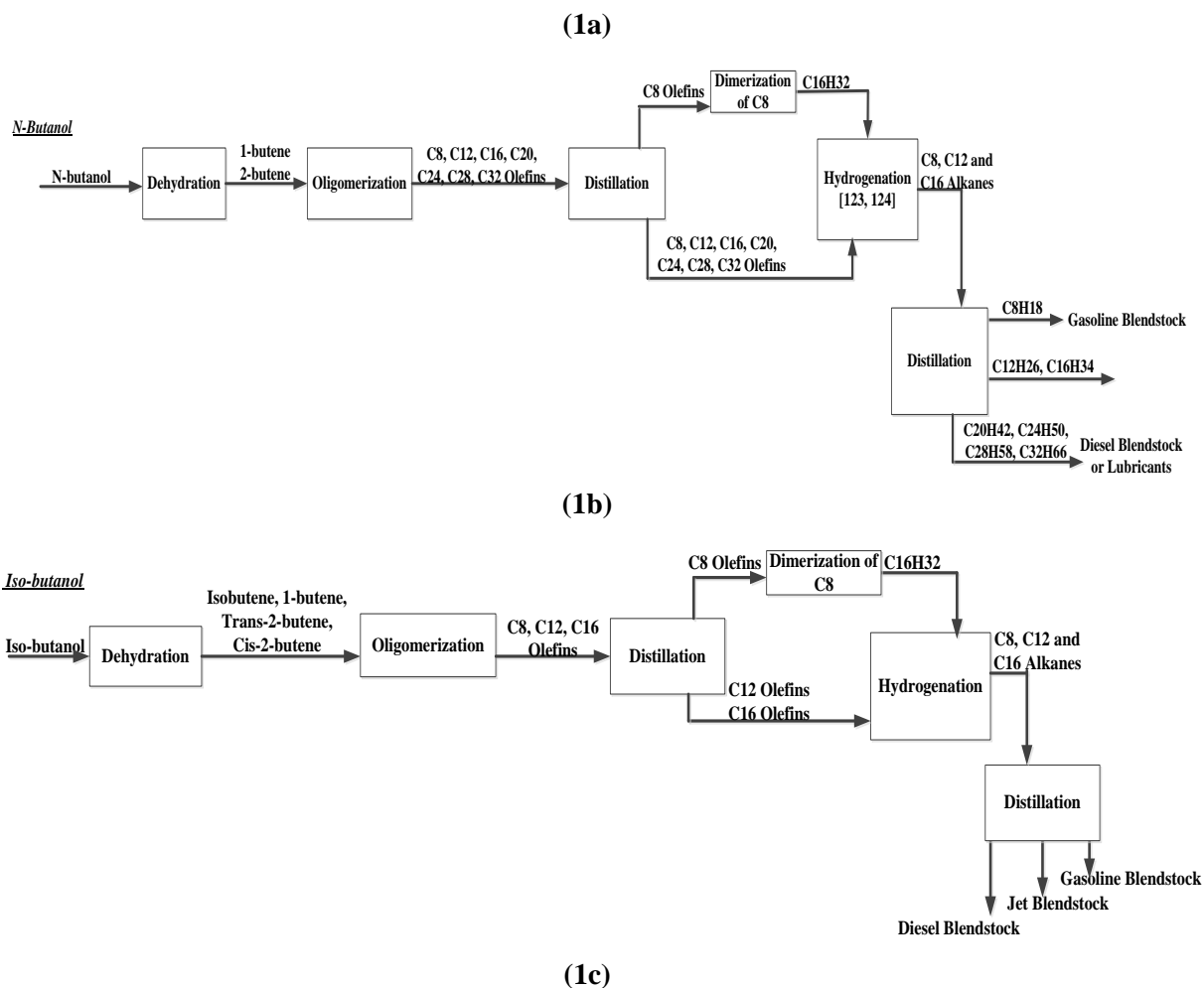


Fig. 1. Alcohol to jet processes: (1a) ethanol to jet; (1b) n-butanol to jet; (1c) iso-butanol to jet [35, 38, 60-63, 65-69, 71, 72, 74, 77-81].

2.1.2 Economic Analysis

To evaluate the production cost for the bio-jet fuel derived from alcohols, the cost of making alcohols, such as ethanol and butanol (n-butanol and iso-butanol) needs to be determined. The techno-economic analysis of both biochemical and thermochemical processes [82, 83] for ethanol production (from starch or cellulosic feedstocks) has been studied extensively [10, 82-90]. Most reports calculate a minimum selling price of the fuel based on a number of economic assumptions. The minimum ethanol selling price for the biochemical conversion of lignocellulosic biomass was recently reported to be \$2.15/gal or \$3.27/gal of gasoline equivalent (GGE) in 2007 US dollars (\$2.76/gal or \$4.18/GGE in 2011 US dollars) [83]. The minimum ethanol selling price for the thermochemical route was reported to be \$2.05/gal or \$3.11/GGE in 2007 US dollars (\$2.5/gal or \$3.8/GGE on 2011 US dollars) [85].

The selling price of butanol from ABE fermentation is projected to be \$0.34/kg (\$1.04/gal) based on the corn feedstock cost of \$79.23/ton [91]. For cellulosic biomass, the price becomes \$3.7/gal or \$4.1/GGE (2011 US dollars) [92]. According to the current market demand and the fluctuation of agricultural prices, cheaper feedstocks such as agricultural waste or algal biomass [93] are desired due to their renewability and non-competition with food. The substrate cost [91], credit for by-products [94], solvent recovery technology [91], and product molar ratio [95] are important factors for economic evaluation of butanol production.

To evaluate the overall ATJ conversion pathway and estimate the commercial feasibility, the economics of the fuel upgrading processes such as dehydration, oligomerization, dimerization, and hydrogenation

also have to be considered. Because these processes are still under development, more research efforts are required to complete this target.

2.1.3 Life-Cycle Assessment

LCA studies for the ATJ process are primarily focused on production of ethanol [96] [97], n-butanol [98], and iso-butanol [92]. The LCA for fuel alcohol production can be categorized into four areas [92]: (1) feedstock (land-use-change), (2) on-site enzyme production, (3) biorefinery process, and (4) biorefinery co-product credits. If different pathways are considered, the biochemical process has slightly different performance from the thermochemical process with respect to GHG emissions, fossil fuel consumption and water consumption. [99].

For n-butanol and iso-butanol conversion, studies have focused on emissions, consumptive water use, global warming potential, and fossil energy consumption [92]. The n-butanol production process releases more direct emissions, such as CO₂, nitrogen dioxide, and sulfur dioxide, than the iso-butanol production process does. CO₂ is produced during the cellulase (or enzyme) production and cellulase seed fermentation, but is largely from combustion [92]. Nitrogen dioxide is formed through high temperature oxidation of the diatomic nitrogen in the combustion air. Sulfur dioxide emissions strongly depend on the amount of sulfuric acid used in the pretreatment process. However, the bio-refining of n-butanol consumes more water than iso-butanol refining does. The biomass feedstock is responsible for most of the global warming potential and fossil energy consumption [92]. Conversion of iso-butanol consumes 5.15 MJ/GGE more fossil fuel than n-butanol conversion does.

The LCA of the ATJ fuel upgrading processes is still unknown and requires more attention in future studies.

2.2 Oil-to-Jet (OTJ) Fuel

In this review, three processes are classified into the OTJ conversion pathway: HRJ, also known as HEFA; catalytic hydro-thermolysis (CH), also termed hydrothermal liquefaction; and hydro-treated depolymerized cellulosic jet (HDCJ), also known as fast pyrolysis with upgrading to jet fuel. Currently, only products from the HRJ pathway have been approved for blending and have a defined ASTM specification.

2.2.1 Process Description

Both HRJ and CH processes employ triglyceride-based feedstocks, but the free fatty acids (FFAs) are produced differently. FFAs in the HRJ process are made by propane cleavage of glycerides, whereas in the CH process FFAs are formed by thermal hydrolysis. The bio-oil in the HDCJ process is produced by pyrolyzing the biomass feedstock. The downstream hydro-treating processes are similar in all three processes. The HRJ, CH, and HDCJ processes are discussed separately below.

2.2.1.1 Hydroprocessed Renewable Jet (HRJ)

HRJ conversion technology is at a relatively high maturity level, is commercially available, and was recently used to produce jet fuel for military flights [57]. HRJ fuel is equivalent to conventional petroleum in properties, but has the advantages of higher cetane number, lower aromatic content, lower sulfur content, and potentially lower GHG emissions [100].

Over the past 60 years, a large variety of catalytic hydrogenation, deoxygenation, hydro-isomerization, and hydrocracking processes have been successfully developed and commercialized. A representative process flow diagram is shown in Figure 2. Renewable fats and oils that have different degrees of unsaturation require the hydrogenation process to completely saturate the double bonds [32]. Catalytic hydrogenation could be used to convert liquid-phase unsaturated fatty acids or glycerides into saturated ones [32] with the addition of hydrogen. The next step is to cleave the propane and produce three moles of FFAs [100]. The glycerol portion of the triglyceride molecule is turned into propane by adding H₂. Alternative route to convert the glycerides to FFAs is thermal hydrolysis [101-103]. Oils and fats that contain mostly triglycerides are converted into three moles of FFAs and one mole of glycerol by

processing the feedstocks with three moles of water. The hydrogen ion from the water is attached on the glycerol backbone and forms one mole of glycerol, where the hydroxyl ion from the water is added to the ester group and produces three moles of FFAs. High temperature (250°C–260°C) is required for water to dissolve in the oil phase. High pressure is also necessary to maintain the reactants in liquid phase. The by-product glycerol has many pharmaceutical, technical, and personal care product applications. The glycerol purification process is energy intensive, adding cost to overall process, but might be offset by glycerol selling value [104].

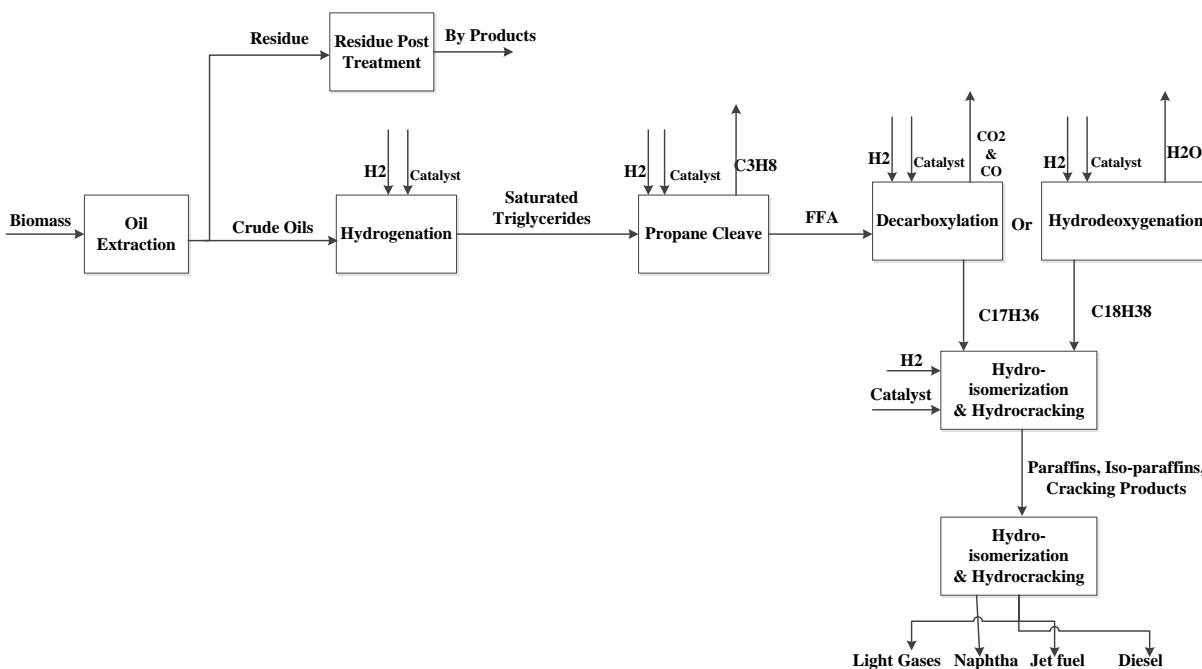


Fig. 2. Hydro-processed renewable jet (HRJ) process

To meet the jet fuel specification, the produced bio-jet fuel has to have not only a high flash point, but also good cold flow properties. Therefore, it is required to hydrocrack and hydro-isomerize the normal paraffins produced from deoxygenation to a synthetic paraffinic kerosene (SPK) product with carbon chains ranging from C_9 to C_{15} [100]. The cracking and isomerization reactions are either concurrent or sequential [32]. Studies have shown that isomerization of straight-chain alkanes occurs first and cracking is a consecutive reaction. The isomerization process takes the straight-chain hydrocarbons and turns them into the branched structures to reduce the freeze point to meet the jet fuel standard [105]. It is accompanied by a hydrocracking reaction, which results in more or less yield from the isomerized species. The hydrocracking reactions are exothermic and result in the production of lighter liquids and gas products. They are relatively slow reactions; thus, most of the hydrocracking takes place in the last section of the reactor. The hydrocracking reactions primarily involve cracking and saturation of paraffins. Overcracking will result in low yields of jet-fuel-range alkanes and high yields of light species ranging from C_1 to C_4 and naphtha ranging from C_5 to C_8 . Both of these are out of jet fuel range and also have lower economic value than diesel or jet fuel.

Bifunctional catalysts containing metallic sites for hydrogenation/dehydrogenation and acid sites for skeletal isomerization via carbenium ions are used in isomerization. In a typical isomerization reaction, normal paraffins are dehydrogenated on the metal sites of the catalyst and reacting on the acid sites to produce olefins protonate with formation of the alkylcarbenium ion. The alkylcarbenium ion is rearranged to monobranched, dibranched, and tribranched alkylcarbenium ions on the acid site. The branched alkylcarbenium ions are deprotonated and hydrogenated to produce the corresponding paraffins [106]. The choice of catalyst will result in variation of cracking at the end of the paraffin molecule and therefore adjust the yield of jet fuel range product [32]. The hydro-isomerization and hydrocracking processes are

followed by a fractionation process to separate the mixtures to paraffinic kerosene (HRJ SPK), paraffinic diesel, naphtha, and light gases.

2.2.1.2 Catalytic Hydrothermolysis (CH)

Catalytic hydro-thermolysis (CH), also named hydrothermal liquefaction, is a novel process that has been developed and patented by Applied Research Associates, Inc., for producing “renewable, aromatic, and drop-in” fuels (known as REDIJet or REDI Diesel) from plant or algal oils [51]. The hydrothermal process (Figure 3), contains a series of reactions, including cracking, hydrolysis, decarboxylation, isomerization, and cyclization, that turn triglycerides into a mixture of straight chain, branched, and cyclic hydrocarbons [107]. The CH reaction is conducted at temperatures from 450°C to 475°C and pressures of 210 bar with water and a catalyst (or without a catalyst). The resulting products—including carboxylic acids, oxygenated species, and unsaturated molecules—are sent to decarboxylation and hydro-treating processes for saturation and oxygen removal. The treated products, ranging from 6 to 28 carbon numbers, contain n-alkanes, iso-alkanes, cyclo-alkanes, and aromatics, which require a fractionation step for separation to naphtha, jet fuel, and diesel fuel. The jet fuel made from the CH process meets ASTM and military (MIL) specifications and has excellent combustion quality, cold flow properties, and stability [50]. Research has shown that through the CH process, bio-jet fuels can be produced from a variety of triglyceride-based feedstocks such as soybean oil, jatropha oil, camelina oil, and tung oil (shown in Table 4) [107, 108].

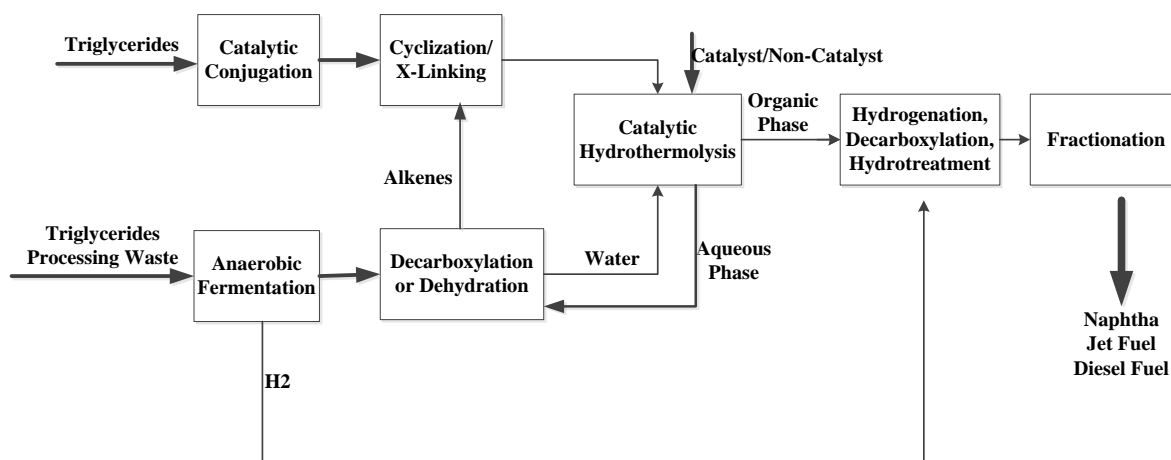


Fig. 3. Catalytic hydro-thermolysis to jet fuel [107, 108].

Table 4. Bio-jet Fuels from the CH Process [107, 108]

	JP-8	From Soybean	From Jatropha	From Tung	From Camelina	From Carinata	MIL-DTL-83133H Spec Requirement
Aromatics	18.8 (vol%)	2.6 (wt %)	10.8 (wt%)	61.7 (wt%)	24.2 (vol%)	16.8 (vol%)	≤ 25.0
Paraffins (normal + iso)	N/A	40.0 (vol%)	32.8 (wt%)	16.2 (wt%)	N/A	N/A	N/A
Olefins	0.8 (vol%)	N/A	N/A	N/A	1.3 (vol%)	1.8 (vol%)	≤ 5.0 (vol%)
Cycloparaffins	N/A	52.0 (vol%)	39.2 (wt%)	16.7 (wt%)	N/A	N/A	N/A
Dicycloparaffins, vol%	N/A	5.9 (vol%)	N/A	N/A	N/A	N/A	N/A
Heat of Combustion, MJ/kg	43.3	43.4	43.4	42.3	42.9	43.2	≥ 42.8
Smoke Point, mm	22	> 30	28	N/A	22	26	≥ 19
Freeze Point, C	-51	< -47	-39	< -66	-54	-57	≤ -47
Flash Point, C	51	> 38	45	39	48	46	≥ 38
Distillation (D2887, D86)	N/A	pass	195-229	187-252	N/A	N/A	N/A
Density, kg/L	0.804	>0.775	0.804	0.839	0.818	0.802	0.775-0.840

	JP-8	From Soybean	From Jatropha	From Tung	From Camelina	From Carinata	MIL-DTL-83133H Spec Requirement
Acid Number, mg of KOH/g	0.003	< 0.010	< 0.010	N/A	0.011	0.012	≤ 0.015
Hydrogen, wt%	13.8	N/A	14	13.3	13.8		≥ 13.4
Viscosity at -40C, cSt	9.9	N/A	N/A	N/A	7.4	6.5	≤ 12.0
Cetane Index	N/A	N/A	43.9	34.2	N/A	N/A	N/A

2.2.1.3 Hydro-treated Depolymerized Cellulosic Jet (fast pyrolysis with upgrading to jet fuel)

Hydro-treated depolymerized cellulosic jet (HDCJ) is a recent technology developed by Kior to convert the cellulosic biomass into renewable gasoline, diesel, and jet fuels [52]. The HDCJ jet fuel has not yet been approved by ASTM. Bio-oils from the pyrolysis process undergo a series of hydro-treating processes to produce jet-fuel-range products. If no further catalytic upgrading is applied, pyrolysis oils undergo hydro-treating and fractionation to form jet blend stocks, as shown in Figure 4. In addition, UOP LLC, PNNL, Ensyn, and Tesoro have been working on upgrading pyrolysis oil to hydrocarbon fuels, including jet fuel, through integrated pyrolysis and hydro-conversion [109-111]. Utilizing feedstocks including corn stover, cane bagasse, switchgrass, guinea grass, algae biomass, and forest residue, this integrated biorefinery system combines commercial RTP (Rapid Thermal Processing) pyrolysis technology with catalytic hydro-conversion. Approximately 42.4–44.2 wt% jet fuel was separated by batch vacuum distillation [109-111].

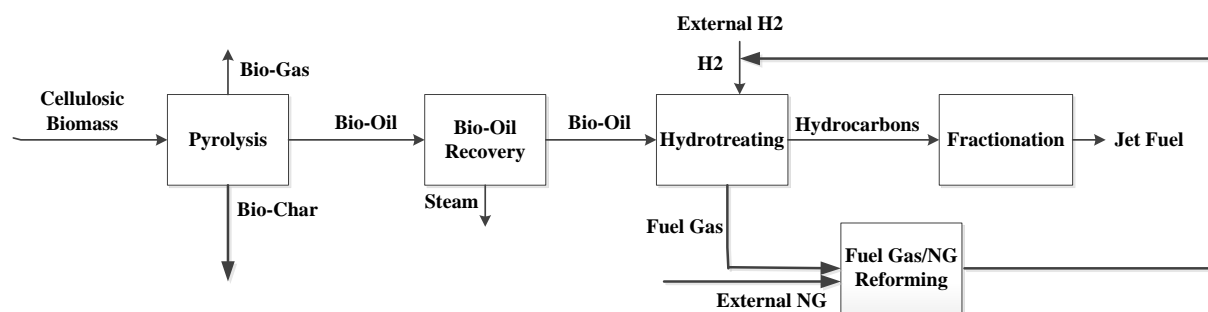


Fig.4. Pyrolysis-to-jet process [52]

2.2.2 Economic Analysis

An economic analysis of HRJ fuel is described in the literature [112]. The HEFA fuel price was found to be \$3.85/gal (\$4.1/gal or \$3.6/GGE on 2011 U.S. dollars) for the plant capacity of 98.28 MM gal/yr and \$4.46/gal (\$4.8/gal or \$4.2/GGE on 2011 U.S. dollars) for the plant capacity of 30.16 MM gal/yr. Additional \$0.27/gal –\$0.31/gal is required to produce maximum jet fuel because of the increased hydrogen use and decreased yields of jet and diesel fuels. The economic analysis of bio-jet fuels from microalgae and pongamia oils are also studied [113]. The minimum selling prices for jet fuels derived from microalgae and pongamia oils are estimated to be \$31.98/gallon or \$28.3/GGE and \$8.9/gallon or \$7.9/GGE (2011 U.S. dollars), respectively. The development of technology and market will decrease the prices to be \$9.2/gallon or \$8.1/GGE and \$6.07/gallon or \$5.4/GGE (2011 U.S. dollars), respectively. Unlike biodiesel production through transesterification, HRJ biofuel production requires hydrogen to hydro-treat the biomass. It is suggested that the capital cost for HRJ is 20% higher than that of biodiesel production due to the hydro-treating process. However, the by-products from HRJ—naphtha, liquefied petroleum gas, propane, and diesel—have more credits than glycerol from the transesterification process [55]. Feedstock costs contribute a significant part of the production cost. For example, 70%–80% of the total production cost for biodiesel production results from the cost of feedstocks [114-117]. Edible and non-edible oils are becoming promising alternatives to biofuel because they are renewable in nature and can be produced locally and in environmentally friendly ways. Table 5 shows the unit oil prices for plant oils, algae oil, waste cooking oil, and pyrolysis oil. Obviously, higher oil yield leads to lower operating cost.

Table 5. Oil Selling Price [118-123]

	Jatropha	Palm	Camelina	Algae	Waste Cooking Oil	Soybean	Rapeseed	Pyrolysis Oil
Oil Price (\$/kg)	0.50	0.79	1.75	3.55	0.115~0.472	1.14	1.72	0.26

By-products from the HRJ process can be upgraded to increase overall yield or sold as a high-value-added co-product. Depending on the conversion technology, the by-products include:

1. Propane, which is created by breaking the carbon backbone of the triglyceride or formed in the fractionation step. It accounts for 4% of the products [100]. The current residential propane price is \$2.48/gal [124].
2. Liquefied natural gas (LNG), which is produced in the product separation step. LNG will increase to 6% if the diesel fuel is cracked down to the jet fuel range [100]. The current price of LNG is \$4.58 per thousand cubic feet [125].
3. Naphtha, which is also formed in the distillation step. The price of naphtha is \$2.03/gal [100].
4. Diesel, which is separated in the fractionation step. The current price of biodiesel is around \$3.64/gal [126].

2.2.3 Life-Cycle Assessment

Several research groups have developed a GHG emissions analysis on a life cycle basis [3, 56, 100, 127]. The GHG emissions for soybean oil are about 40% to 80% of those of conventional jet fuel (89 gCO₂e/MJ for Jet A fuel) [56], resulting from the soybean yield, N₂O emissions from fertilizer, liming emissions, and H₂ requirements in the hydro-treating process. The GHG emissions increase when land use change is considered. One study shows low soybean yield from tropical rainforest results in 800% more emissions than conventional jet fuel [56]. The emissions of the palm oil to jet fuel process are about 30% to 40% of those of conventional jet fuel production processes, resulting from palm fresh-fruit-bunch yield per acre, farming energy, methane emissions from palm oil-mill effluent treatment, H₂ requirements in the hydro-treating process, and hydro-processing fuel yield. GHG emissions increase to the range of 40% to 800% of those of conventional jet fuel when accounting for land use change [3]. For rapeseed oil, the emissions are around 45% to 87% of those of conventional jet fuels [3] and increase to 87% to 147% when considering land use change. For jatropha oil, the emissions are 36% to 52% of those from conventional jet fuel, and N₂O emissions represent more than 20% of the total emissions. Zero emissions from land use change are assumed due to the assumption that marginal land will be used. Other research shows the emissions from jatropha OTJ conversion were 40 gCO₂e/MJ of fuel produced [127], approximately 45% of that of conventional jet fuel. For algal oil, the emissions range from 16% to 220% of those from conventional jet fuel. The wide range results from the uncertainty of emissions from CO₂ injection and dewatering and drying processes [3]. For salicornia oil, the emissions range from 35% to 76% of those from conventional jet fuel [3]. The GHG emissions of liquid fuel production via fast pyrolysis of cellulosic biomass have been studied by researchers at Argonne National Laboratory [128]. When hydrogen is generated from natural gas and bio-char is used to support the process energy, the GHG emissions are reduced by 45% relative to conventional fuels. When hydrogen is produced from reforming of pyrolysis oil and bio-char is applied as the fertilizer, the GHG emissions are reduced by 103% relative to conventional fuels [128].

2.3 Gas-to-Jet (GTJ) Fuel

The GTJ pathway presented here describes the conversion processes that turn biogas, natural gas, or syngas into bio-jet fuel. The F-T and gas fermentation processes are classified in this pathway and are reviewed here.

2.3.1 Process Description

2.3.1.1 Fisher Tropsch Biomass to Liquid (FT-BTL) Process

The F-T process is capable of producing liquid hydrocarbon fuels from syngas. F-T fuels are typically free of sulfur and contain very few aromatics compared to gasoline and diesel, which leads to lower emissions when used in jet engines [12]. Some recent studies point out that the use of the F-T technology to convert biomass to synthetic fuels may provide a promising carbon-neutral alternative to conventional diesel, kerosene, and gasoline [129-131]. The process reviewed here is the FT-BTL process.

In the FT-BTL process (Figure 5), biomass feedstocks are first dried to reduce the particle sizes during pretreatment [132]. Multiple gasification technologies exist to convert the biomass to syngas. In a high-temperature (slagging) gasification process, the dried biomass is pressurized and converted into raw synthesis gas during gasification at temperatures around 1300C in the presence of high purity oxygen and steam. A combustor is included to provide heat to dry the biomass. The direct-quench syngas cooling system next to the gasifier removes ash and tars. A water-gas-shift system after quench is applied to adjust the $H_2:CO$ ratio to 2.1:1 [132]. NREL has conducted an investigation on indirect gasification and tar reforming [85]. In this design, the endothermic gasification process is indirectly-heated by the circulation of hot olivine and the material in the gasifier is fluidized by the steam. Gasification occurs at atmospheric conditions and at 880°C. The syngas is further conditioned such that the residual tars, methane and light hydrocarbons are reformed to syngas in a fluid catalytic cracker. Water gas shift also occurs in the reformer. Compared to the high temperature gasification, this design has the benefits of energy self-sufficient, improved capital cost associated with the smaller process scale, and neutral electrical energy [86].

After syngas is produced, it is polished with zinc oxide and an activated carbon sorbent and compressed to 25 bar, the F-T operating pressure. H_2 used in hydro-processing stage can be purified through a pressure swing adsorption. The syngas is then processed by F-T synthesis to produce liquid fuel [129, 131], as illustrated in Figure 5.

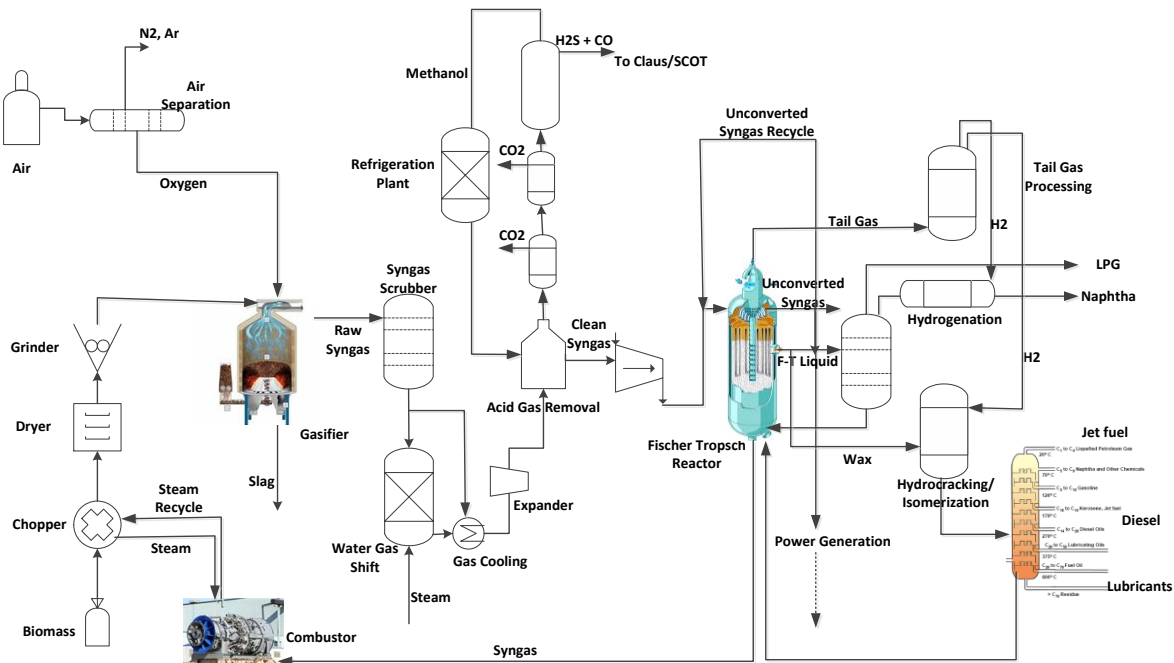


Fig. 5. FT-BTL process [133]

F-T synthesis is a set of catalytic processes for converting syngas into liquid hydrocarbons. There are two well-known F-T operating modes [134]; high temperature and low temperature. The high-temperature

process runs at 300°–350°C with iron-based catalysts. Gasoline and linear low-molecular-mass olefins are produced in this process. The low-temperature process operates at 200°–240°C with either iron or cobalt catalysts. Linear waxes produced in the low-temperature process have higher molecular mass than those produced in the high-temperature process. In the F-T process, the products range from methane to long-chain hydrocarbons. Besides alkanes and alkenes, oxygenated compounds such as alcohols, aldehydes, and carboxylic acids are also formed. Aromatics and ketones are also produced in the high temperature process. The F-T process is a highly exothermic process; therefore, the heat of reaction has to be removed quickly to avoid overheating and deactivating the catalyst and also to prevent production of undesired methane [135]. Traditional F-T catalysts, such as iron-, cobalt-, nickel- and ruthenium-based catalysts, have been extensively studied in the literature [130, 134, 136-143]. Product selectivity and product distribution depend strongly on the operating temperature and the partial pressure of the gases that contact the catalyst.

After F-T synthesis, a portion of the unconverted syngas is returned to the F-T reactor, and part of it is sent to the acid gas removal system [131]. The remaining portion flows into the power generation area, providing power for the air separation unit [131]. Conventional refinery processes, such as hydrocracking, isomerization, hydrogenation, and fractionation, can be applied to upgrade the F-T synthesis product to high-quality, low-aromatic, and almost zero-sulfur-content fuels [144]. Hydrocracking/isomerization is used to convert the wax into lighter products with shorter chain length and lower boiling points. Products from the hydrocracking/isomerization reactor are heated and distilled to produce jet fuel, diesel fuel, and lubricants. Hydrogenation is applied to produce naphtha from the F-T liquid. The F-T tail gas, which contains H₂, water, methane, CO, CO₂, nitrogen, argon, and heavier hydrocarbons, is recycled back to the syngas generation system. H₂ in the tail gas can be purified through the pressure swing absorber and can be further used in the hydrocracking/isomerization process.

2.3.1.2 Gas Fermentation Process

Instead of catalytically upgrading F-T syngas to bio-jet fuel, it is also possible to ferment syngas to liquid biofuels (Figure 6). If lignocellulosic biomass is used as the feedstock, it is first converted into syngas via gasification. The cooled syngas can be fermented to ethanol or butanol by acetogenic bacteria [145]. The acetogenic bacteria *Clostridium* is used to consume CO and H₂ to produce ethanol and 2,3-butanediol [145]. Other products such as acetate, acetone, isopropanol, and butanol can be produced by other biosynthetic pathways with different microbe strains [146]. The mixed alcohol, ethanol, or 2,3-butanediol can be upgraded into jet fuel via the ATJ technology described in Section 2.1.2, which includes dehydration, oligomerization, distillation, and hydrogenation processes [147]. Gas fermentation has several potential advantages. It is able to produce more products than the traditional biochemical or thermochemical pathways can [148], and it has an overall energy efficiency of 57%, while the F-T process has a relative overall energy efficiency of 45% [146]. The process requires lower temperature and pressure, as well as less expensive enzymes [148]. Gas fermentation can convert not only energy crops and typical agricultural wastes, but also municipal and industrial organic waste [148].

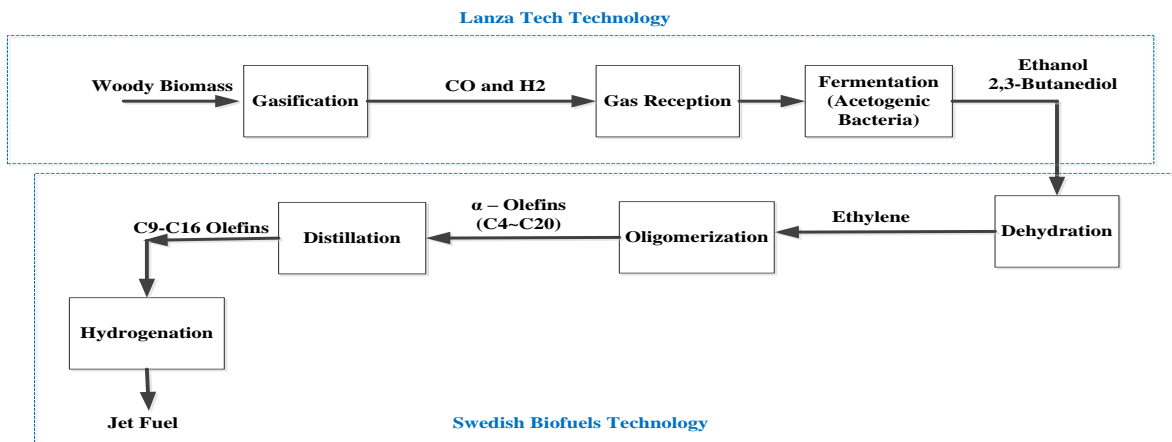


Fig. 6. Gas fermentation to bio-jet fuel

2.3.2 Economic Analysis

The production cost of BTL jet fuel has been reported based on BTL diesel production due to the similarity of the processes [12]. The feedstock price, as shown in the report, has a significant effect on the cost of the BTL fuel. High-cost energy crops contribute about 70 % more to the cost of the fuel than high-cost forestry residues and wastes [12]. In addition, production costs are reduced with the reduction of the conversion cost and improvement of the energy crop yield. It is estimated that the conversion cost will be reduced by 26 % from 2012 to 2026 [12]. The unit production cost of BTL is expected to be higher than that of CTL due to the lower energy efficiencies with smaller plants and the higher capital cost of gasification [56]. The jet fuel production cost of CTL is estimated as \$1.70 to \$2.04/gal (\$2.26 to \$2.72/gal on 2011 U.S. dollars), whereas for CBTL it is estimated as \$1.99/gal to \$2.34/gal (\$2.65 to \$3.11/gal on 2011 U.S. dollars) [56]. The temperature of gasification also has a high impact on the cost analysis of the BTL F-T process [90, 149]. A low-temperature gasifier has several constraints, such as the limitation of reaction kinetics and the formation/flow of slag [90]. Based on processing 2,000 metric tons per day of corn stover, the total capital investment for the high-temperature (1,300°C), slagging, entrained flow gasification process, including feedstock handling, solids feeding, gasification, amine scrubbing, sour water-gas-shift, pressure swing adsorption, F-T synthesis, hydrocracking, and air separation/power generation, is \$500 million (2007 basis) [149]. The total capital investment for the low temperature (870°C), non-slagging, direct fluidized bed gasification process is \$610 million. With the same capacity, high-temperature (1,300°C) indirect gasification has total capital investment of \$516 million (2007 basis) [85]. Compared to the pyrolysis and biochemical processes, gasification has the highest capital cost [150]. Followed by catalytic F-T synthesis and hydro-processing to naphtha-range and distillate-range liquid fractions, the product values for the high temperature and low temperature direct gasifiers are \$4.50/GGE and \$5.00/GGE (\$5.50/GGE and \$6.10/GGE on 2011 US dollars), respectively. Tijmensen et al. [151], pointed out that the pretreatment, gasification with oxygen, and gas cleaning sections account for approximately 75% of total capital cost. The production cost of F-T liquids in this study ranged from \$9/GJ to \$16/GJ (\$1.86/gal to \$3.30/gal on 2011 US dollars).

2.3.3 Life-Cycle Assessment

In the syngas production and fuel synthesis processes, the GHG emissions considered are [152] (1) CO₂ emissions from gasification, F-T synthesis, fossil fuel combustion, and venting from natural gas production; (2) methane emissions from fugitive plant and pipeline emissions, incomplete combustion, and coal bed methane releases; and (3) N₂O emissions from fuel combustion and the cultivation of biomass. The F-T CTL and F-T GTL processes have high life-cycle GHG emissions [152, 153]. The F-T CTL process has GHG emissions 10% higher than those of conventional jet fuel with carbon capture and 120% higher without carbon capture. GHG emissions from the F-T BTL process are 92%–95% less than those of conventional jet fuel because the feedstock for F-T BTL, either woody biomass or forestry residues, has a very low contribution [12]. This is also because 48% of the energy consumed for the conversion processes, either gasification or F-T synthesis, comes from the biomass itself [12]. The life-cycle GHG emissions from the use of corn stover, forest residue, and switchgrass are 9.0, 12.2, and -2.0 gCO₂e/MJ, respectively (with a soil carbon-change credit, the CO₂ sequestration arising from land use change dominates the GHG emissions), which are about 10%, 14%, and -2% of those of conventional jet fuel, respectively [3]. It is also suggested that identifying strategies and technologies, such as carbon sequestration, co-production of fuels and power, co-processing of coal and biomass, and improved vehicle technology will help reduce GHG and other emissions from the F-T process [154]. When switchgrass is used as the feedstock, the WTW GHG emissions range from 11.9 gCO₂e/MJ to 26 gCO₂e/MJ without soil carbon sequestration and from -1.7 gCO₂ to -4.4 gCO₂e/MJ with soil carbon sequestration [3]. HRJ fuel has higher GHG emissions, about 62%–92% more than F-T BTL [21] due to higher fertilizer and chemical use. The effect of carbon capture and storage on climate, estimated in terms of radiative forcing

of the production and utilization chains of the F-T fuel based on GHG emissions, has been studied [155]. It is concluded that without carbon capture and storage, the climate impacts of F-T fuel from peat are 30%–40% lower than from petroleum fuels. With carbon capture and storage, the climate impacts of peat-based F-T fuels are 50%–84% lower than petroleum diesel.

2.4 Sugar-to-Jet Fuel

The biological and catalytic conversion of sugars to hydrocarbons provide a biochemical route to the production of liquid transportation fuels and chemicals [17, 43-48, 156, 157]. According to reports by DOE's Office of Energy Efficiency & Renewable Energy Bioenergy Technologies Office [39, 40], STJ fuel can be processed via two pathways:

1. Catalytic upgrading of sugars or sugar intermediates to hydrocarbons: sugars are separated from biomass (e.g., milled corn stover) through a series of chemical and biochemical processes and upgraded into hydrocarbon fuels through aqueous phase reforming (APR). The process has been operated by companies such as Virent and Virdia. The jet fuel produced from the process has been tested in AFRL and passed the relevant specifications of Jet A1 fuel.
2. Fermentation of sugars to hydrocarbons: the sugars from biomass are fermented directly to hydrocarbon fuels or hydrocarbon intermediates, recovered, purified, and further upgraded to drop-in hydrocarbon fuels. This process has been operated by companies such as LS9 and Amyris, and the renewable jet fuel produced by the process from a sugarcane feedstock has been used in an Embraer E195 jet operated by Azul Brazilian Airline [158].

2.4.1 Process Description

The STJ processes include (1) catalytic upgrading of sugars to hydrocarbons, (2) fermentation of sugars to hydrocarbons, and (3) sugar-to-sugar intermediate and upgrading to fuel.

2.4.1.1 Catalytic Upgrading of Sugars to Hydrocarbons

Lignocellulosic sugars are typically produced by pretreatment and enzymatic hydrolysis of biomass feedstocks. A certain level of purification and concentration of biomass sugars is often needed before catalytically upgrading sugar to hydrocarbons, which converts sugar or its intermediates to a range of hydrocarbon molecules and hydrogen in an APR process. The hydrocarbon molecules are separated in a fractionation process to jet, gasoline, and diesel fuels. Bio-derived chemicals, such as para-xylene for polyethylene-terephthalate-saturated polyester polymers, are also produced [40] and can be credited as co-products. Closed loop processes that recover and recycle the unreacted species are significant to improve the process economics [17], but separation of the product mixtures can be technically challenging.

Virent's BioForming platform is one example of a process that turns the plant sugars into high-energy hydrocarbon mixtures (Figure 7) [44, 48, 144, 159]. Following the pretreatment and fractionation processes, lignocellulosic biomass is converted and separated to cellulose, hemi-cellulose, and lignin. Lignin, in this process, is sent to the combustor to provide process heat. Using enzymatic or acid hydrolysis, the fractionated cellulose and hemicellulose are turned into sugars with five and six carbons. The carbohydrates are converted into polyhydric alcohols via hydrogenation [160] or short-chain oxygenates via hydrogenolysis [161]. The key step in the BioForming platform is APR. Through APR, the product stream from the hydro-treating step is reacted with water over a proper heterogeneous catalyst at temperatures of 450 to 575 K and pressures of 10 to 90 bar. The APR reaction includes reforming to produce hydrogen, dehydrogenation of alcohols/hydrogenation of carbonyls, deoxygenation, hydrogenolysis, and cyclization [161]. Products that form in APR are hydrogen, carbon dioxide, alcohols, ketones, aldehydes, alkanes, organic acids, and furans [162]. Hydrogen produced from APR will support the hydro-treating process before the APR step and hydro-refining processes after the APR step. The lighter alkanes from APR, such as C₁–C₄ hydrocarbons, are sent to the combustor to provide additional process heat [163].

Based on the available open literatures, there are three potential routes to convert the oxygenates from the APR step into jet-fuel-range hydrocarbons. As shown in Figure 7, the first route is acid condensation, which turns the oxygenates into alkanes, iso-alkanes, and aromatics with a zeolite ZSM-5 catalyst. The reactions include dehydration of oxygenates to alkenes, oligomerization of the alkenes to heavier alkenes, cracking, cyclization and dehydrogenation of heavier alkenes to aromatics, alkane isomerization, and hydrogen-transfer to form alkanes [162, 164, 165]. The heavier species of the products can be distilled and blended into jet fuel. The second route is direct catalytic condensation over multifunctional solid-base catalysts [81, 166]. There are several condensation reactions occurring: (1) aldol condensation to produce a β -hydroxyketone or β -hydroxyaldehyde, (2) dehydration of β -hydroxyketone or β -hydroxyaldehyde to produce a conjugated enone, (3) hydrogenation of the conjugated enone to produce ketone or aldehyde, and (4) removal of hydroxyls by dehydration/hydrogenation or hydrogenolysis to form alkanes [81, 166]. The products from this route are mostly in the jet fuel range. The third route is to convert the oxygenates from APR to alkanes and alkenes via dehydration and hydrogenation-dehydration reactions. The alkenes are oligomerized to produce kerosene with solid phosphoric or zeolite catalysts [167, 168].

To obtain high selectivity to fuels, a catalyst that helps generate hydrocarbons with low oxygen content and with the appropriate amount of branching, cyclic, and aromatic content is needed [17]. The catalyst should be able to deal with a wide range of sugars and contaminants, including sulfur, nitrogen and ash. In addition, the ideal catalyst should be able to handle lignin and its decomposed products with high carbon efficiency and long catalyst lifetime [17].

Researchers at the University of Wisconsin-Madison developed a two-stage process that converts sugar derived from biomass into 2,5-dimethylfuran (DMF) [169]. The fructose, obtained directly from biomass or by isomerizing of glucose, was dehydrated to form 5-hydroxymethylfurfural (HMF) by removing five oxygen atoms over an acid catalyst. HMF was then turned into DMF through hydrogenolysis over a CuRu catalyst. The resulting DMF has higher energy density by 40% and a higher boiling point by 20 K than ethanol, and it is not water soluble [169]. This study created a new path for the production of DMF as a replacement for traditional petroleum transportation fuels.

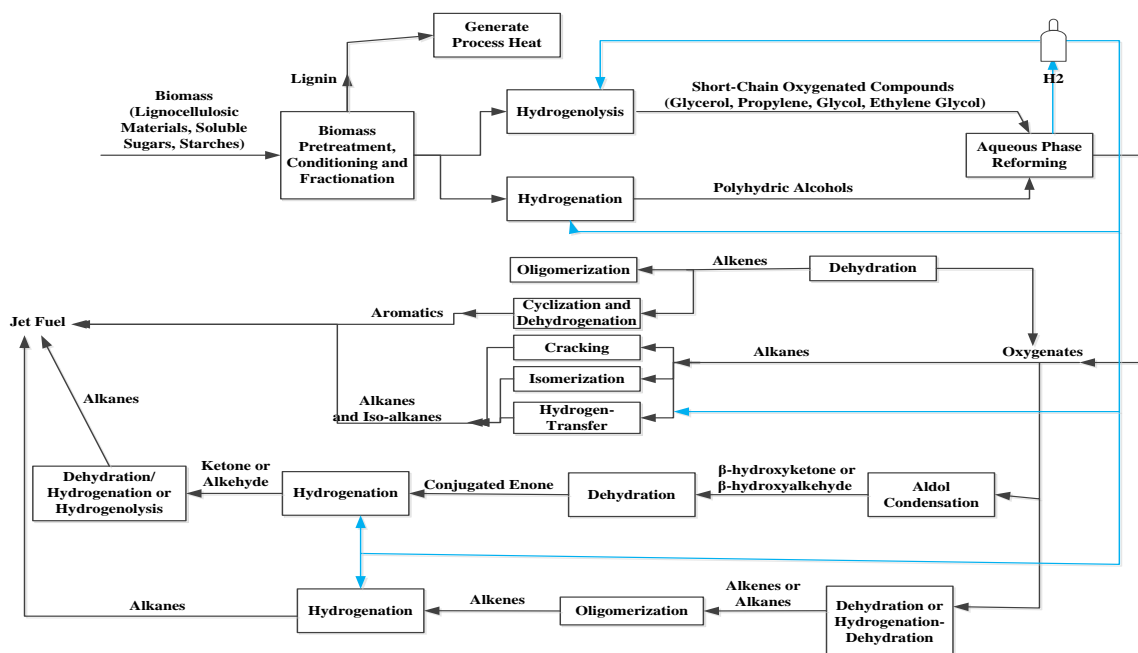


Fig. 7. Catalytic upgrading of sugars to jet fuel (Virent BioForming Process)

Note: Blue line represents the hydrogen supply

2.4.1.2 Direct Sugar to Hydrocarbons (DSH)

In the direct sugar-to-hydrocarbons process, biomass cell walls are broken down and hemicellulose sugars are released. After enzymatic hydrolysis, which removes solid materials, liquid sugars are often concentrated by removing 50% of the water. Hydrocarbon intermediates are produced by processing concentrated sugars through an aerobic fermentation process using fed-batch or continuous fermentation. The resulting products are then sent to a phase separation stage to recover the hydrocarbon fuels [39].

The processes developed by Amyris and LS9 successfully transforms sugars to hydrocarbon fuel [170, 171]. There are two pathways to produce isopentenyl pyrophosphate (IPP), the precursor of liquid fuel: the mevalonic acid (MVA) pathway and the deoxyxylulose-5-phosphate (DXP) pathway [172]. The three-carbon compound pyruvate derived from glycolysis of glucose is turned into three moles of acetyl-CoA. The mevalonate pathway employs three moles of acetyl-CoA and produces the five-carbon IPP [17]. The DXP pathway produces IPP via condensing pyruvate and D-glyceraldehyde-3-phosphate from glycolysis [17]. The DXP pathway has higher carbon efficiency (83%) than the MVA pathway does (56%) [17]. The terpenes, assembled by condensing IPP and its isomer dimethylallyl pyrophosphate, represent the candidates of biologically-derived fuel [17]. Large terpenes can be cracked to liquid fuel and the branched olefins can be hydrogenated to isoparaffins [17, 171]. Figure 8 shows an example of sugar fermentation to hydrocarbons in which the sugar syrup is processed through the MVA and converted into artemisinic acid, isopentenyl pyrophosphate, and jet/gasoline precursors. The artemisinic acid is then turned into an anti-malarial drug, and isopentenyl pyrophosphate is further transformed into farneseny pyrophosphate and C₁₅ isoprenoids, which are the precursors of diesel and chemicals [170]. The fermentation waste could be optionally processed with anaerobic digestion to reduce the effluent. After purification, through downstream hydro-processing, the jet/gasoline precursors can be turned into bio-jet fuel.

An engineered *E. coli* fatty acid pathway has been developed to produce fatty esters, fatty alcohols, and waxes from sugars [17, 173]. Through combining the thioesterase-catalyzed hydrolysis of fatty acyl-ACP, with fatty acyl-CoA-synthase-catalyzed reactivation of the fatty acid carboxylate group, fatty acyl-CoA was converted from fatty acid metabolism. Fatty esters were produced by applying an acyltransferase with an alcohol-forming pathway; fatty alcohols were produced from fatty acyl-CoAs by expressing fatty acyl-CoA reductases; and wax was produced through the fatty alcohol pathway [173]. Through the pathway consisting of acyl-acyl carrier protein reductase and an aldehyde decarbonylase, the C₁₃–C₁₇ mixtures of alkanes and alkenes, part of the component of jet fuel, are produced from these intermediates of fatty acid metabolism [171]. This invention, developed by LS9, enables the conversion of biomass into jet fuels without the need for chemical conversion technologies such as distillation or hydrogenation.

Scientists in Berkeley have developed a novel process that integrates ABE fermentation and chemical catalysis to selectively produce jet, diesel, and gasoline products from lignocellulosic and cane sugars [73]. Glycerol tributyrate has been used to efficiently separate acetone and n-butanol from ethanol and to remove several inhibitors of fermentation found in acid-pretreated lignocellulosic biomass, such as furfural, *p*-coumaric acid, and ferulic acid. Acetone and butanol from ABE fermentation are converted into ketone through a condensation reaction over K₃PO₄ and a palladium catalyst. The resulting products, a C₁₁ compound with a ketone in the middle, can be fed into the refinery infrastructure as a feedstock to produce renewable jet fuel [73].

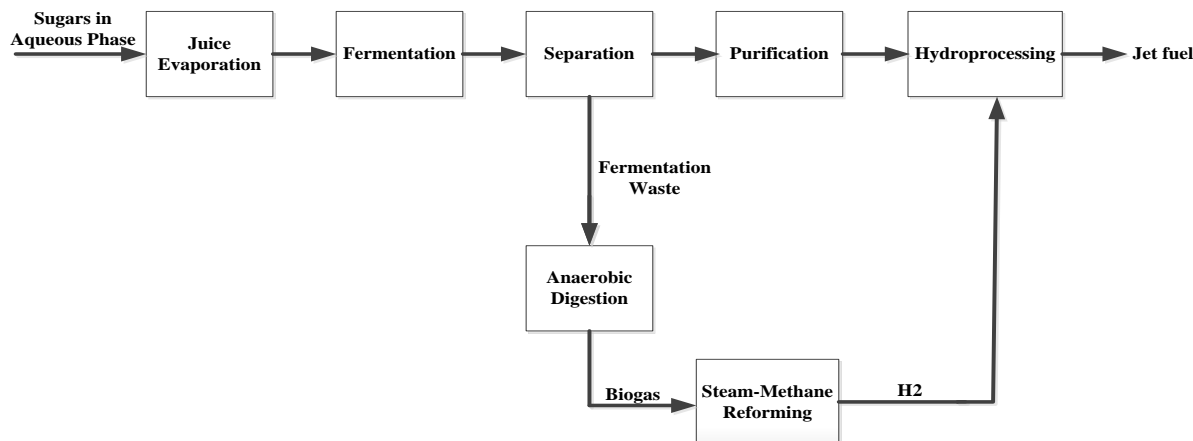


Fig. 8. Direct sugar-to-jet fuel

2.4.2 Economic Analysis

When analyzing the process economics of STJ, separation of the sugar and sugar intermediates from other compounds needs more attention [17]. Separation of decomposed biomass slurries sometimes accounts for 50%~70% of capital and operating costs at a biorefinery [174]. Decreasing viscosities, increasing fluxes, and avoiding formation of precipitants are ways to increase the efficiency of separation at high temperatures [174]. NREL and Virent are currently conducting a process economic analysis for Virent's BioForming technology [144]. Four main process steps, (1) pretreatment/fractionation, (2) hydrogenation, (3) APR, and (4) acid catalyzed dehydration/condensations, are considered to affect the production cost significantly [144]. Additionally, researchers from Iowa State University and the University of Wisconsin-Madison conducted a techno-economic study of DMF and HMF production [175]. Based on the process capacity of 300 metric ton/day of fructose and an operating period of 20 years, the resulting minimum selling prices for HMF and DMF were estimated to be \$5.03/gal (\$6.2/gal or \$4.8/GGE on 2011 US dollars) and \$7.63/gal (\$9.4/gal or \$9.9/GGE on 2011 US dollars), respectively. The cost of the copper-ruthenium-carbon catalyst used in the DMF process might play an important role in the final production cost. This study provides a single point on the TEA associated with catalytic upgrading of a pure expensive clean sugar to a single product at a small scale. Other comparative analysis shows that the production of levulinic acid from biomass costs approximately \$4.31/GGE [176]. For the DSH pathway, the techno-economic analysis is conducted to evaluate the selling price of bio-jet fuel derived from sugarcane, resulting in \$7.16/gallon (\$7.2/gal or \$6.3/GGE on 2011 US dollars) for the base case and \$4.00/gallon (\$4.0/gal or \$3.5/GGE on 2011 US dollars) with the development of the technology and the market [113]. NREL in support of the NABC efforts, in collaboration with Virent and Amyris, is also conducting process economics studies for a direct sugar to fuel process [144]. The target is to find the low-cost routes for biomass hydrolysate streams and low-cost mitigation strategies for fermentation inhibitors that are compatible with the current state of the art. Future work should consider the catalytic upgrading of biomass-derived sugars to a slate of fuel components, specifically jet fuel.

2.4.3 Life-Cycle Assessment

The Institute for International Trade Negotiations conducted a study of life-cycle GHG emissions of bio-jet fuel produced from sugarcane sugars based on the Amyris process parameters [43]. The results showed that the life-cycle GHG emissions are around 15 gCO₂e/MJ, an approximate 82% reduction compared with conventional Jet A/A-1 fuels [43]. However, sugarcane could induce land use change, which was not considered in the study above. The GHG emissions associated with sugarcane production and transport, according to the study, are primarily dominated by farm input and the emissions of N₂O from the soil, which contribute 32 gCO₂e/MJ and 45 gCO₂e/MJ, respectively [41]. This research helps improve the knowledge of the carbon footprint of a renewable aviation fuel derived from sugarcane.

3 Summary of all bio-jet fuel production pathways

Production yields, including intermediate and jet fuel yields, production costs and GHG emissions for the conversion technologies reviewed in this work are summarized in Table 6 for yields (details explained in Supplementary Materials), Table 8 for production cost and Figure 9 for GHG emission.

Feedstock is the most important parameter when considering the commercial feasibility of bio-jet fuel production. Agricultural and forest feedstocks as well as algal biomass are major feedstocks for producing alcohol fuels, able to provide large amounts of alcohols for converting into jet fuel. Plant oils, animal fats, waste cooking oils, algal oil, and pyrolysis oils are the predominant feedstocks for oil-related conversion processes such as HRJ, CH, and HDCJ. Agricultural and forest residues can serve as major feedstocks for producing syngas or biogas. There is an abundance of sources of sugars (lignocellulosic or grain sugar) to ferment or synthesize to jet fuels via the STJ process. From the variable feedstocks, the sum of all the intermediates per dry ton biomass for each pathway is demonstrated in Table 6, using energy basis, i.e., GGE per dry ton biomass (BDT). Based on these literature data, ethanol from syngas fermentation has the highest reported yield (306.8 GGE/BDT) due to the 90% carbon conversion. On the other hand, algal oil has relatively low yield (22.5–29.9 GGE/BDT) because of the low oil content reported. Table 6 not only reports the yields of intermediates, but also summarizes the jet fuel yield after upgrading intermediates to finished products. The jet fuel yields demonstrate the jet fuel production from literature reported data or several assumptions for the calculating intermediates to jet productions. Detailed analyses can be found in the Supplementary Materials. For example, the jet fuel yield from palm seed results from the calculation of the product yield from palm oil through deoxygenation and hydro-treating processes. The jet fuel yield from corn stover derived isobutanol comes from the estimation of the product yield through dehydration, oligomerization and hydro-treating processes. For consistent purpose, the units are normalized from volumetric basis (gallon) to energy basis (GGE) by dividing the lower heating value (LHV) of the products (Table 7) by the LHV of gasoline. The yield values provide a general idea of the pathway/feedstock that most final products can be obtained from. The HRJ process with palm seed as the feedstock has the highest conversion from intermediate to final products (67.8%) due to the high carbon conversion. The CH process with jatropha seed as the feedstock has the lowest intermediate-to-jet conversion (8.0%) because most of the carbon distributes out of the jet fuel pool.

The maturity of a conversion process controls the process economics. FT-to-jet fuel (as an example of GTJ) has first been proved by ASTM as a promising technology. Product selection, which leads to the yield of jet fuel, is strongly dependent upon the operating temperature, partial pressure of syngas, and the applied catalyst. The HRJ process is also an approved process, representing one of the OTJ technologies. The use of hydrogen and selection of a catalyst contribute to a significant part of the production costs. ATJ and STJ processes are at the R&D stage, and may be the next processes being approved. The jet fuel product yield, which depends on the catalyst or enzyme used, has attracted more and more interest and driven more research efforts.

The production cost for intermediates and final jet fuel from each pathway are summarized in Table 8. If the feedstock costs, financial assumptions, and analysis methodologies are not normalized, the cost numbers cannot be compared consistently. Both volumetric basis and energy basis units are presented in the table for consistency. All the cost numbers are adjusted to 2011 US dollars. Both the feedstock cost and conversion technology contribute a significant portion of each production cost. The STJ pathway has higher intermediate cost due to the early stage of technology development and the HDCJ (one of the OTJ technologies) has a lower intermediate cost because the selling price of pyrolysis oil is reported to be very low in the literature. As seen in the table, only HRJ and DSH processes have some reported numbers for jet fuel blendstock production cost. HRJ fuel can be produced for \$4.3–\$9.2/gal (equivalent to \$3.8–\$8.1/GGE in 2011 US dollars) [112, 113], which is expected to decrease once the technology can be further improved. STJ fuel through DSH process was evaluated to be \$7.2/gal (equivalent to \$6.3/GGE in 2011 US dollars) [113] and this can be reduced when the technology and market are further developed. As seen in Table 8, the production costs from intermediates to final products increase slightly for HRJ process and increase significantly for DSH process. The credits obtained from the co-products in the HRJ

process lowers the cost of the upgrading processes from intermediates to jet fuel and benefits the entire conversion process. The cost estimates for the other upgrading processes are not available and require future investigation.

The GHG emissions of jet fuels from the reviewed pathways are compared in Figure 9, using gCO_2/MJ basis. The GHG emission of ATJ pathway is currently not available, so only the data for process to make alcohols is reported here. A potential penalty, expected for upgrading alcohols to jet fuels, is roughly estimated based on the environmental impact of the refinery processes, including dehydration, oligomerization and hydro-treating. It is presented as a dashed line box, shown in Figure 9. GHG emissions primarily come from the farm input, land use change, and biorefinery processes. The GHG emissions from HRJ pathways range from 16% to 800% of those from conventional jet fuel depending on the feedstocks as well as coproducts [3]. For F-T BTL, the life-cycle GHG emissions are -2 – 12.2 $\text{gCO}_2\text{e}/\text{MJ}$ from the use of corn stover, forest residue, and switchgrass, approximately -2% – 14% of those of conventional jet fuel [3]. The STJ process through the direct sugar-to-hydrocarbons process contributes 15 $\text{gCO}_2\text{e}/\text{MJ}$ GHG emissions [43], about an 82% reduction from conventional jet fuel. Apparently the GHG emissions are reduced when using the bio-jet fuel and STJ pathway has the highest reduction.

Table 6. Production Yields from Various Biomass Feedstocks Using Various Pathways

	Pathway	Biomass	Intermediate Yield [GGE/BDT]	Jet Fuel ^A Yield [gal/BDT]/ [GGE/BDT]	Ref.
Alcohol to Jet	Ethanol to Jet	Dry Mill	---	---	[38, 61, 63, 64, 71, 83, 85, 177, 178]
		Corn ^Q	77.5	39.6/44.7	
		Unrefined Sugar ^Q	13.9	7.1/8.0	
		Switchgrass ^Q	55.9	28.5/32.2	
	N-butanol to Jet (Dehydrated over a Pd/C-K ₃ PO ₄ catalyst)	Corn Stover ^R	120.9	74.1/83.7	[73, 179-185]
		Corn Fiber ^R	57.2	34.2/38.6	
		Glucose ^R	112.7	69.0/78	
		Wheat Straw ^R	112.7	69.0/78	
		Liquefied Corn Starch ^R	112.7	69.0/78	
		Switchgrass ^R	101.6	62.3/70.4	
		Barley Straw ^R	118.1	72.4/81.8	
		Sweet Potato Slurry ^R	53.5	32.8/37.1	
		Whey Permeate ^R	120.9	74.1/83.7	
		Corn Fiber ^R	57.2	10.0/11.3	
	Glucose ^R	112.7	19.5/22		
	Wheat Straw ^R	112.7	19.5/22		
	Liquefied Corn Starch ^R	112.7	19.5/22		
	Switchgrass ^R	101.6	17.6/19.9		
	Corn Stover ^R	120.9	21.0/23.7		
	Barley Straw ^R	118.1	20.5/23.2		
Sweet Potato ^R	53.5	9.3/10.5			
Whey Permeate ^R	120.9	21.0/23.7			
Isobutanol to Jet	Dry Mill	---	---	[38, 68, 71, 72, 77, 92, 133, 178, 181]	
	Corn ^S	163.6	51.9/58.6		
	Unrefined Sugarcane ^S	29.4	9.3/10.5		
	Switchgrass ^S	118.4	14.4/16.3		
Methanol to Jet	Woody Biomass ^T	79.2	45.4/51.3	[83, 186-189]	
Oil to Jet	HRJ	Vegetable Oil	---	---	[3, 21, 100, 190-199]
		Palm Seed ^{E,U} (22% Oil)	58.3	41.9/47.3	
		Rapeseed ^{E,U} (45% Oil)	127.9	75.2/85	
		Soybean ^{E,U} (18% Oil)	49.8	29.9/33.8	
		Jatropha Seed ^{E,U} (35% Oil)	92.0	59.9/67.7	
		Camelina Seed ^{E,U} (29% Oil)	85.9	47.2/53.3	
		Camelina Seed ^{E,U} (41% Oil)	121.4	66.2/74.8	
		Algal ^{E,U} (25% Oil)	61.9	44.3/50	
		Salicornia Seed ^{E,U} (28.2% Oil)	61.6	45.0/50.8	
	CH	Soybean (18% Oil)	28.7	7.6 ^B /8.6	[3, 107, 200]
		Jatropha Seed (35% Oil)	56.0	8.9 ^B /10.1	
		Tune Seed (40.4% Oil)	102.1	15.2 ^B /17.2	
	HDCJ	Dry Wood ^V	93.5	41.1 ^B /46.4	[201-209]
		Corn Stover ^V	71.8	36.4 ^B /41.1	
		Switchgrass ^V	74.8	37.9 ^B /42.8	
		Sugarcane Bagasse ^V	62.3	31.6 ^B /35.7	
		Algae 18% Oil Content ^V	22.5	11.4 ^B /12.9	
Algae 24% Oil Content ^V		29.9	15.2 ^B /17.2		
Forest Residue Low ^V		74.8	37.9 ^B /42.8		
Forest Residue High ^V		81.1	41.1 ^B /46.4		

	Pathway	Biomass	Intermediate Yield [GGE/BDT]	Jet Fuel ^A Yield [gal/BDT]/[GGE/BDT]	Ref.
Gas to Jet	F-T to Jet	Natural Gas	---	156.4/176.7	[3, 55, 131, 210-215]
		Coal ^J	---	84.1 ^H /95	
		Hardwood ^I	---	63.9/72.2	
		Switchgrass	---	---	
	Gas Fermentation	Natural Gas ^{O, Q}	306.8	139.5 ^C /157.6	[38, 61, 63, 64, 68, 71, 72, 77, 133, 143, 145, 146, 177, 178, 181, 216-218]
				204.5 ^D /231	
		Natural Gas ^{P, Q}	259.1	117.8 ^C /133.1	
				172.7 ^D /195.1	
		Biomass ^Q	65.8	29.9 ^C /33.8	
				43.8 ^D /39.8	
		Hardwood ^Q	77.3	35.2 ^C /39.8	
				51.5 ^D /58.2	
		Biomass Feedstock ^Q	52.7	23.9 ^C /27	
			35.1 ^D /39.7		
		21.3 ^C /24.1			
		31.2 ^D /35.2			
Sugar to Jet	Catalytic Upgrading	Corn Stover ^{F, W}	91.8	52.7/59.5	[162, 219-222]
		Sugarcane Bagasse	62.8	49.0/55.4	
		Hardwood ^{F, W}	75.3	41.7/47.1	
		Switchgrass ^{F, W}	81.5	48.1/54.3	
		Sugarcane ^{F, X}	65.8	44.5/50.3	
		Sugar Beet ^{F, X}	54.8	37.1/41.9	
		Cellulosic Mass ^{K, Y}	26.9	13.8/15.6	
	Corn Stover ^{L, W}	91.8	21.9/24.7	[81, 175]	
	Direct Sugar to Jet	Corn Stover ^{M, W}	91.8	36.9/41.7	[162, 223]
		Corn Stover ^{N, Z}	56.4	18.5/20.9	[172, 220]

- Notes: ^A Unless otherwise stated "Jet Fuel" is defined as C₉-C₁₅ n-alkanes
^B Jet range based off of boiling point
^C Using Ethanol to Jet Pathway to create Jet Fuel C₉-C₁₅ alkanes
^D Using Isobutanol to Jet Pathway, Jet Fuel C₉-C₁₅ alkanes
^E Uses the decarboxylation pathway
^F Catalytic Upgrading Using Virent Pathway
^H Coal to Liquid Fuel (CTL), unknown ranges of gasoline, diesel, and jet
^I The average of several design cases for hardwood gasification
^J The average of six notable sources for the production of CTL fuel from coal
^K Catalytic Upgrading Condensation to HMF to Jet
^L Catalytic Upgrading non-fermentation of biomass
^M Direct Sugar to Jet Mevalonic (MVA) Pathway
^N Direct Sugar to Jet Deoxysylulose-5-phosphate (DXP) Pathway
^O 90% of Carbon Conversion to Syngas
^P 76% of Carbon Conversion to Syngas
^Q Starting Intermediate: Ethanol
^R Starting Intermediate: A:B:E (Acetone:Butanol:Ethanol)
^S Starting Intermediate: Ethanol→ Isobutanol
^T Starting Intermediate: Methanol
^U Starting Intermediate: Triglyceride Oil
^V Starting Intermediate: Liquid Pyrolysis Oil
^W Starting Intermediate: Glucose : Xylose
^X Starting Intermediate: Sucrose
^Y Starting Intermediate: Fructose
^Z Starting Intermediate: Glucose : Xylose : Fructose
--- Data not available

Table 7. Lower Heating Values of the Intermediates

Lower Heating Value	MMBTU/gal	Ref.
Gasoline heating value	0.12	[83]
Ethanol heating value	0.08	[83]
Acetone heating value	0.08	[224]
n-butanol heating value	0.10	[95]
Isobutanol heating value	0.10	[92]
Methanol heating value	0.06	[224]
Palm oil heating value	0.12	[225]
Rapeseed oil heating value	0.13	[225]
Soybean oil heating value	0.13	[225]
Jatropha oil heating value	0.12	[226]
Camelina oil heating value	0.14	[227]
Algal oil heating value	0.12	[228]
Salicornia oil heating value	0.12	[3]
Tung oil heating value	0.12	[229]
Pyrolysis oil heating value	0.07	[230]
Glucose heating value	0.09	[231]
Xylose heating value	0.08	[83]
Sucrose heating value	0.09	[83]
Fructose heating value	0.09	[232]
Jet fuel heating value	0.13	[20]

Table 8. Production costs of Jet Fuel from Various Pathways

Category	Pathways	Intermediate	Interm. Cost ^A (\$/gal) [(\$/GGE)]	Final jet fuel cost (\$/gal) [(\$/GGE)]	Ref.
ATJ	Ethanol to Jet	Ethanol ^B	2.5-2.6 (3.8-4.0)	Not Available	[83, 85]
	n-Butanol to Jet	N-butanol ^B	3.7 (4.1)		[92]
	Iso-Butanol to Jet	Isobutanol ^B	3.6 (4.0)		[92]
	Methanol to Jet	Methanol	1.5 (3.0)		[233]
OTJ	HRJ	Bio-Oil ^C	4.3-8.5 (4.0-8.2)	4.3-9.2 (4.0-8.5)	[100, 112, 113, 234]
	CH	Bio-Oil ^D	1.7-4.3 (1.6-3.9)	Not Available	[113, 235]
	HDCJ	Pyrolysis Oil	1.0-1.5 (1.8-2.6)		[118, 201, 236]
GTJ	F-T to Jet (BTL)	Syngas derived diesel	6.4-6.7 (6.0-6.2)	Not Available	[56]
	Gas Fermentation	Ethanol from syngas fermentation	2.8-3.1 (4.3-4.8)		[237, 238]
STJ	Catalytic Upgrading of Sugar to Jet	HMF and DMF	6.2-9.4 (4.8-9.9)	Not Available	[175]
	DSH	Hydrocarbons ^E	4.6 ^F (4.4)	7.2 (6.6)	[113, 239]

Note: ^A The cost numbers are inflated to 2011 U.S. dollars using the industrial inorganic Chemical Index for SRI Consulting [240]

^B The alcohol intermediates are produced from cellulosic biomass

^C Soybean and algal oils are selected for the lower and higher end bio-oils

^D Jatropha and soybean oils are selected for the lower and higher end bio-oils

^E Pentadecane

^F Target value of the product

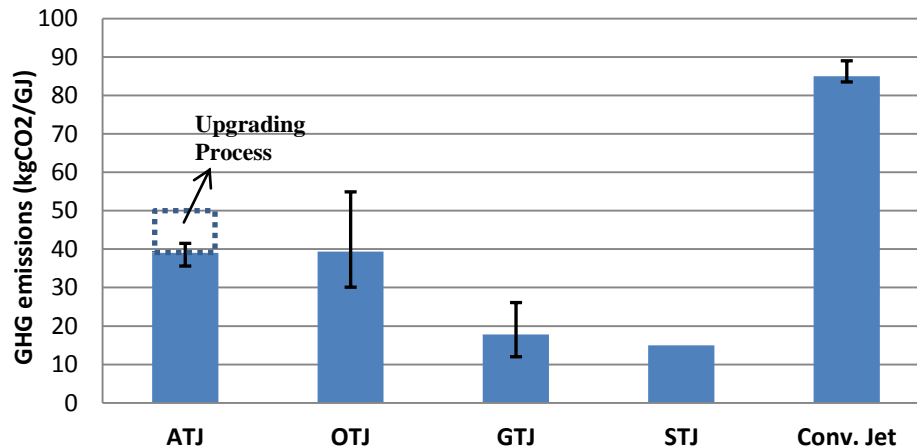


Fig. 9. GHG emissions of jet fuel from various pathways
([3, 12, 14, 21, 33, 43, 55-57, 92, 127, 128, 199, 241-243])

Note: ^A For ATJ pathway, the higher and lower end uncertainties represents GHG emissions of n-butanol and ethanol, respectively

^B For OTJ pathway, the higher and lower end uncertainties represents GHG emissions of rapeseed and palm oils, respectively

^C For the GHG emissions of OTJ and GTJ pathways, without land use change is considered

^D For GTJ pathways, switchgrass is selected as the feedstock; without soil carbon sequestration is considered

4 Conclusion

The issues of jet fuel cost, energy supply, energy security, and aviation emissions have driven the development of aircraft and engine technologies throughout the history of flight. Sustainable biomass-derived bio-jet fuel represents a major opportunity to resolve these issues. Many conversion technologies that turn biomass into jet fuels have been developed, and some of them are commercially viable. In this review, most of the current technologies have been classified into four major categories: ATJ, OTJ, GTJ, and STJ. Each category has been described and reviewed with regard to feedstocks, upgrading processes, production costs when available, sustainability, and commercial readiness.

Sustainable bio-jet fuel not only brings environmental benefits for aviation, but helps the development of a new industry. There is still a considerable way to proceed before renewable aviation fuels become economically viable. Through the combination of expertise of the aviation industry, government, biofuel companies, agriculture organizations, and academic systems, along with encouragement from regional banks, progress is being made toward an optimal process that utilizes the most effective feedstock sources, is amenable with current infrastructure, and produces renewable aviation fuels.

Acknowledgement

The work was sponsored by the Research Center for Energy Technology and Strategy, National Cheng Kung University and also supported by the U.S. Department of Energy, Bioenergy Technologies Office., under Contract No. DE-AC36-08GO28308 with the National Renewable Energy Laboratory.

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