

Analysis of Integrated Tropical Biorefineries

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Executive Summary

This report evaluates the current technological status of biorefinery component technologies for the conversion of locally grown biomass into fuels (ethanol, gasoline, bio-diesel, renewable diesel, jet fuel, etc.) and electricity in the State of Hawaii. The examined conversion technologies can be categorized into three platforms: biochemical, chemical, and thermochemical conversions. The technological status (lab-, pilot-, demo- and commercial scale), the required inputs (feedstock, thermal and electrical energy) and production outputs (fuel and electricity) and costs, as well as the energetic process efficiency and known drawbacks of each conversion technology were assessed qualitatively and quantitatively. Salient points from this assessment are summarized in Tables ES1 and ES2. Three scenarios defined by the quantities of feedstock that could be produced on 15,000, 36,000 and 100,000 acres of land were considered for supplying an island-scale biorefinery with locally grown biomass (see Table ES3 for prospective crops). The potential for fuel and electricity production as well as advantages and drawbacks of each platform conversion technology are summarized below based on the medium scale scenario (36,000 acres of land).

1. Biorefinery based on a biochemical platform

With the exception of conversions involving sugars derived from lignocellulosic feedstocks, the investigated biochemical platforms are well established and yield, cost and conversion efficiency data are readily available. However, assumptions and projections were made to accommodate the integration of an anaerobic digester into each biochemical platform technology. The combustion of biogas to generate process heat and electricity allows the starch platform technology to become thermally self-sufficient and to generate excess electricity that can be fed into the grid. The lignocellulosic- and sugar platform do not rely on biogas combustion to be thermally self-sufficient. However, their output of excess electricity is enhanced by integrating anaerobic digestion into the conversion process. Consequently, all investigated biochemical platforms are thermally autonomous and, moreover, produce an excess amount of electricity.

On a 36,000 acre basis, the biochemical conversion of banagrass to ethanol yields the largest annual amount of ethanol (61 MGY) followed by sugar cane (34 MGY), corn (32 MGY) and cassava (31 MGY). The lignocellulosic tree crops *Eucalyptus* and *Leucaena* both yield about 12

MGY due to their lower annual productivity. The largest amount of annual surplus electricity is generated by the sugar cane process (173 GWh) trailed by banagrass (105 GWh), corn (69 GWh) and cassava (40 GWh). Again, the tree crops *Eucalyptus* and *Leucaena* yield less surplus electricity (20 GWh). The investment cost projections for the biochemical technologies on a 36,000 acre basis show the lowest capital requirements for a corn to ethanol facility (1.2 M\$/MGY), followed by cassava (1.7 M\$/MGY), sugar cane (2 M\$/MGY) and lignocellulosic biomass (6.9 M\$/MGY). Only the corn to ethanol process offers the possibility to produce a valuable co-product in the form of Dried Distillers Grain (DDG). The availability of locally produced DDG in the State has the potential to supply a range of animal feeding operations and thus to increase the production of locally produced meat products.

In the case of corn and cassava, non-starchy biomass leftover from the harvest (i.e. corn stover and above ground cassava biomass) could potentially be used to generate further electricity through combustion. Alternatively, the biomass could be used to augment the soil after composting. Other processing technologies such as pyrolysis or gasification are imaginable assuming that the processing capacities are already existent and in close proximity.

2. Biorefinery based on chemical platform

The transesterification of vegetable oils to biodiesel is a process that is well understood and has been commercially adapted throughout the world. Although the technology offers high conversion efficiency, low yields of oil bearing crops are a limitation. *Jatropha*, the only terrestrial oil crop investigated in this report, yields about 114 gal/acre/year of biodiesel or 4.1 MGY on a 36,000 acre basis [50]. Although there is a general lack of large scale production data for algae and systems for fuel production are currently unproven [34], current estimates suggest that 67 MGY of vegetable oil could be produced on 36,000 acre of land. Capital cost requirements, pond contamination, oil harvest and purification still represent large economic and technological hurdles.

3. Biorefinery based on pyrolysis platform

Pyrolysis is a highly versatile process that can be optimized for the production of char, liquids (oils / tars) or gases depending on the reactor configuration and reaction conditions. 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 [1]. Nonetheless, a number of companies are now offering 'off-the-shelf' fast-pyrolysis units at scales up to 400 t/d dry input [2]. Although, due to a lack of operational commercial facilities and the proprietary nature of cost and efficiency data, limited information is available.

Considering a land area of 36,000 acres for supplying biomass to a fast-pyrolysis reactor (Table 3.4), the greatest mass yield of bio-oil can be attributed to banagrass (460,000 tonnes, ~2,500 GWh_{th}), followed by the tree crops *Leucaena* and *Eucalyptus* with 250,000 tonnes and a corresponding energy content of 1,400 and 1,500 GWh_{th}, respectively. The capital cost of a fast-pyrolysis reactor operating at this scale is on the order of \$100 million and the production cost is in the range of \$100-700 per tonne of bio-oil using recent estimates [1, 3-6].

Bio-oil from fast-pyrolysis may be suitable as a direct replacement for LSFO and coal in existing power stations after relatively minor upgrading steps (e.g. filtration or blending) [1]. For use in stationary diesel engines, the bio-oil would probably require more extensive upgrading and the use of additives which may not prove to be cost effective at present [1, 5]. Bio-oil also has the potential to be upgraded by hydro-treatment or other catalytic processes to produce replacement transportation fuels (gasoline, diesel and jet-fuel). However, these methods have yet to be demonstrated at commercial scale or proven to be financially viable [1].

4. Biorefinery based on the gasification platform

A biorefinery based on the gasification platform can produce transportation fuels, bio-ethanol, electricity, SNG, hydrogen and other chemical products such as fertilizers, wax, etc. Generally, any type of crop, agriculture waste, forest waste, and municipal solid waste (MSW) as well as solid residues generated from biochemical/chemical processes, such as fermentation residue, bagasse, etc., can be converted with this platform.

Banagrass, the lignocellulosic energy crop with the largest yield, produces about 774,000 tonnes of dry matter annually on a 36,000 acre plot (~2,000 tonnes per day). This is enough feedstock to supply a gasification plant with approximately 400 MW thermal input. The crop yields of

Leucaena and *Eucalyptus* are about 50% of banagrass and, consequently, the facilities would be proportionally smaller. Depending on the desired output, two scenarios present themselves (based on 400 MW_{th} input, banagrass):

- 1) FT synthesis: Based on Swanson's analysis for a LT (low temperature) scenario [7], about 37 MGY of gasoline equivalent and 152 GWh electricity can be produced annually. This would replace about 10 % of Hawaii's motor gasoline consumption and 1.5% of the State's electricity consumption (refer to Figures 3.4 and 3.5). The investment cost of a plant of this scale is estimated to be about \$500 million and the fuel production cost estimates are ~\$4.80 per gallon of gasoline equivalent [7].
- 2) Ethanol synthesis: He et al. [8] projects an annual output of approximately 63 MGY of ethanol after syngas-to-ethanol conversion. The estimated capital and fuel cost (based on 2011) are \$130 million and \$1.38 per gallon, respectively. No net-output of electricity is projected and the plant is thermally self-sufficient.

Larger scale scenarios (>1,000 MW_{th} input), as projected with the 100,000 acre scenario, are anticipated to require feedstock densification in intermediate facilities (e.g. through torrefaction, pelletization or pyrolysis) prior to gasification to reduce transportation cost and improve storage and handling properties. At this time, small-scale scenarios involving gasification and fuel synthesis (e.g. banagrass on 15,000 acres, or about 170 MW_{th} input) appear economically unfavorable.

Table ES 1. Qualitative technology overview

	Technology status ¹	Products	Feedstock	Co-products
Ethanol from biochemical route				
Sugar	C	EtOH	sugar	electricity
Starch (corn)	C	EtOH	starch	electricity, DDG
Cellulosic	D	EtOH	fiber	electricity
Gasification				
Heat	C	process heat	fiber	none
Combined Cycle	D/C	electricity	fiber	process heat
IC Engine	D/C	electricity	fiber	process heat
FT-Synfuels	D/C	Syngas, FT-gasoline, FT-diesel	fiber	process heat, electricity
Pyrolysis				
Bio-oil production	D/C	bio-oil	fiber	none
Charcoal production	D/C	charcoal	fiber	none
Bio-oil production for transportation fuels	P/D	Gasoline, diesel, jet-fuel	fiber	none
Combustion	C	electricity	fiber	process heat
Biodiesel via transesterification of veg.oil	C	biodiesel	veg.oil, terrestrial or aquatic origin	oil cake
Renewable diesel via hydrotreating of veg. oil	D	renewable diesel	veg.oil, terrestrial or aquatic origin	none
Anaerobic digestion				
Methane	C	Methane gas	sugars, starches, protein, fats, org. acids, alcohols	nutrient-rich water and digestate (sludge)
Power	C	electricity		
Torrefaction	D	torrefied wood	fiber	none
¹ P = pilot scale, D = demonstration scale, C = commercial scale				

Table ES 2. Qualitative technology and crop overview of the output from various platforms based on annual crop yields at three scales scenarios for a biorefinery

Feedstock/ yield/HHV	Biorefinery platform	Key Data	15,000 acres	36,000 acres	100,000 acres
Sugar Cane ^a 50 tonne/acre 4.7 MJ/kg ^b	Biochem. conversion (sugar platform)	Input: feedstock, M tonnes	0.75	1.80	5.00
		Output: EtOH, Mgal. (GWh _{th})	14 (345)	34 (839)	95 (2344)
		Output: electricity, GWh	72	173	480
		Capital cost estimate, \$/gal. capacity ^h	2.7	2.0	1.5
Corn ^c 8 tonne/acre 16.0 MJ/kg	Biochem. conversion (starch platform)	Input: feedstock, M tonnes	0.12	0.28	0.79
		Output: EtOH, Mgal. (GWh _{th})	13 (317)	32 (770)	87 (2,153)
		Output: electricity, GWh	28	69	190
		Capital cost estimate, \$/gal. capacity ^h	1.8	1.2	0.9
Cassava ^d 20 tonne/acre 6.7 MJ/kg	Biochem. conversion (starch platform)	Input: feedstock, M tonnes	0.30	0.72	2.00
		Output: EtOH, Mgal. (GWh _{th})	13 (316)	31 (769)	87 (2149)
		Output: electricity, GWh	17	40	110
		Capital cost estimate, \$/gal. capacity ^h	2.2	1.7	1.2
Banagrass ^e 21.5 tonne/acre 18.0 MJ/kg	Biochem. conversion (lignocellulosic platform)	Input: feedstock, M tonnes	0.32	0.77	2.15
		Output: EtOH, Mgal. (GWh _{th})	25 (614)	61 (1505)	169 (4181)
		Output: electricity, GWh	44	105	292
		Capital cost estimate, \$/gal. cap.	no data	6.9	no data
	Fast-pyrolysis	Output: Bio-oil, M tonnes (GWh _{th}) ^j	0.19 (1037)	0.46 (2490)	1.29 (6916)
		Output: electricity, GWh ^k	0	0	0
		Production cost estimate, \$/t ^l	100-700	100-700	100-700
		Total capital investment, M\$ ^m	30-80	~106	~295
	Gasification ethanol synthesis ^f	Output: EtOH, Mgal. (GWh _{th})	26 (639)	63 (1553)	176 (4339)
		Output: electricity, GWh	0	0	0
		Production cost estimate, \$/gal.	1.72	1.38	1.13
		Total capital investment, M\$	72	134	275
	Gasification FT-synthesis ^g	Output: Gasoline eq., Mgal. (GWh _{th})	15 (645)	37 (1548)	102 (4299)
		Co-output: electricity, GWh	63	152	421
		Production cost estimate, \$/gal.	n.a	4.80	n.a
		Total capital investment, M\$	291	548	1114
Eucalyptus ^e 10 tonne/acre 19.0 MJ/kg	Biochem. conversion (lignocellulosic platform)	Input: feedstock, M tonnes	0.15	0.36	1.00
		Output: EtOH, Mgal. (GWh _{th})	12 (292)	28 (700)	79 (1945)
		Output: electricity, GWh	20	49	136
		Capital cost estimate, \$/gal. capacity	no data	6.9 \$/MGY	no data
	Fast-pyrolysis	Output: Bio-oil, M tonnes (GWh _{th}) ⁿ	0.10 (595)	0.25 (1428)	0.70 (3966)
		Co-output: electricity, GWh ^k	0	0	0
		Production cost estimate, \$/t ^l	100-700	100-700	100-700
		Total capital investment, M\$ ^m	15-38	~50	~140
	Gasification ethanol synthesis ^f	Output: EtOH, Mgal. (GWh _{th})	12 (297)	30 (722)	82 (2018)
		Output: electricity, GWh	0	0	0
		Production cost estimate, \$/gal.	2.46	1.62	1.33
		Total capital investment, M\$	42	80	161
	Gasification FT-synthesis ^g	Output: Gasoline eq., Mgal. (GWh _{th})	7 (300)	17 (720)	47 (1999)
		Output: electricity, GWh	29	71	196
		Production cost estimate, \$/gal.	n.a	n.a	4.80
		Total capital investment, M\$	171	318	648
Leucaena ^e 10 tonne/acre 19.5 MJ/kg	Biochem. conversion (lignocellulosic platform)	Input: feedstock, M tonnes	0.15	0.36	1.00
		Output: EtOH, Mgal. (GWh _{th})	12 (292)	28 (700)	79 (1945)
		Output: electricity, GWh	20	49	136
		Capital cost estimate, \$/gal. capacity	no data	6.9	no data
	Fast-pyrolysis	Output: Bio-oil, M tonnes (GWh _{th}) ^o	0.10 (610)	0.25 (1463)	0.70 (4064)
		Output: electricity, GWh ^k	0	0	0

		Production cost estimate, \$/t ^f	100-700	100-700	100-700
		Total capital investment, M\$ ^m	15-38	~50	~140
	Gasification ethanol synthesis ^f	Output: EtOH, Mgal. (GWh _{th})	12 (297)	30 (722)	82 (2018)
		Output: electricity, GWh	0	0	0
		Production cost estimate, \$/gal.	2.46	1.62	1.33
		Total capital investment, M\$	42	80	161
	Gasification FT-synthesis ^g	Output: Gasoline eq., Mgal. (GWh _{th})	7 (300)	17 (720)	47 (1999)
		Output: electricity, GWh	29	71	196
		Production cost estimate, \$/gal.	n.a	n.a	4.80
		Total capital investment, M\$	171	318	648
Jatropha 114 gal/acre 33 MJ/L	Trans- esterification	Input: feedstock, Mgal.	1.7	4.1	11.4
		Input: thermal, GWh	2.2	5.2	14.5
		Input: electric, GWh	0.1	0.3	0.9
		Output: EtOH, Mgal. (GWh _{th}) ^p	1.7 (59)	4.1 (142)	11.4 (395)
		Capital cost estimate, \$/gal. capacity	2.2	1.5	1.0
Algae 1,852 gal/acre 33 MJ/L	Harvest and Trans- esterification	Input: feedstock, Mgal.	28	67	185
		Input: thermal, GWh	202	485	1348
		Input: electric, GWh ^r	61	146	404
		Output: Biodiesel, Mgal. (GWh _{th}) ^q	28 (963)	67 (2310)	185 (6417)
		Capital cost estimate, \$/gal. capacity	no data	no data	no data

Notes:

In all cases it was assumed that there is no change in the mass conversion or efficiency with scale; only the costs are influenced by scale (when information was available). With the exception of the transesterification platform, all conversion platforms are thermally self-sufficient.

^a based on historic production data in Hawaii, burned and cropped.

^b assuming $HHV_{\text{sucrose}} = 16.5\text{MJ/kg}$ and $HHV_{\text{bagasse}} = 19.2\text{MJ/kg}$ and 13.5% sucrose, 13% fibre.

^c shelled corn, assuming two harvests per year with 160 bushel/acre.

^d fresh tuber weight, 25% starch content.

^e dry, 0 wt% moisture.

^f Ref. [8].

○ Assumed that 1 kg or 1.27 L or 0.33 gal EtOH can be produced from 4.01 kg biomass; or 1 tonne biomass can produced 82 Gal EtOH;

○ €100 million capital cost for the plant with a scale of 1,800 tonne biomass input per day, or 60 million gal EtOH output,

○ Converted to dollars where €1.0 = \$1.3

^g Ref. [7].

○ Conversion of 179 L FT liquids per tonne biomass input, $HHV=152\text{MJ/gal}$ of FT liquid.

○ 707 MJ electricity produced per tonne of dry biomass, converted to 196 MWh.

○ Basic scale: 2,000 t/d biomass input, 32.3 GGE output/year, and \$498 million for capital cost; scale factor: 0.7.

^h Capital investment for anaerobic digestion and CHP is not included. Refer to Table 2.2 for a cost estimate.

- ^j mass conversion of 60% dry basis for grasses [1], energy content was estimated by assuming a fuel-based net efficiency of 65% giving a HHV of 19.3 MJ/kg for dry bio-oil, cf. Table 2.4.2.6. It should be noted that the energy conversion is estimated as no data is available for banagrass.
- ^k electrical output/input is zero as it is assumed that for a fully integrated and optimized commercial scale facility the fuel-gas produced during the process would have sufficient energy to generate the on-site electricity requirements, cf. Section 2.4.2.1.3, sub-section U2.
- ^l production cost data (estimates) vary widely depending on the source (due to the different assumptions and bases used), a ballpark range is \$100-700/t bio-oil output when the feedstock cost is \$0-100 per dry tonne; cf. Section 2.4.2.1.7.
- ^m capital cost data (estimates) are only available for a scale of ~220 t/d dry input (80,000 t/y, year = 365 days) at \$9-20 million, and 1,000 t/d dry input at \$50 million; therefore capital costs are based on multiples of 220 or 1,000 t/d dry input units; cf. Section 2.4.2.1.7.
- ⁿ mass conversion of 70% dry basis for woody biomass, energy content was estimated by assuming a fuel-based net efficiency of 75% giving a HHV of 20.4 MJ/kg for dry bio-oil, cf. Table 2.4.2.6.
- ^o mass conversion of 70% dry basis for woody biomass, energy content was estimated by assuming a fuel-based net efficiency of 75% giving a HHV of 20.9 MJ/kg for dry bio-oil, cf. Table 2.4.2.6.
- ^p based on 114 gallons per year per acre.
- ^q based on 1850 gallons per year per acre.
- ^r includes electrical needs for harvest, drying, extraction and transesterification (based on Xu et al. [9]).

Table ES 3. Energy crop overview

Feedstock	Typical yield ^a	Primary Product(s)	Nutrient requirements ^b	Total water requirements ^b	Agricultural Readiness in Hawaii?
	[tonne/acre/year]	[-]	[kg N/ha]	[mm]	[-]
Sugarcane	50 ^{c,h}	sugar fiber	100-150 ^m	1,500-1,800 ^m	yes
Corn	8 ^d	starch fiber	157 ⁱ	600 ^j	no
Cassava	20 ^e	starch fiber	100 ^k	1,200-1,500 ^l	no
Banagrass	21.5 ^{e,h}	fiber	100-150 ^m	1,500-1,800 ^m	no
<i>Leuceana</i>	10 ^{f,h}	fiber	0 ^{m,p}	500-1,000 ^{m,p}	no
<i>Eucalyptus</i>	10 ^{g,h}	fiber	0 ^p	> 1,000 ^{m,p}	yes
<i>Jatropha</i>	114 ⁿ gal/acre/year	oil	n.a.	n.a.	no
Algae	1,850 ^o gal/acre/year	oil	n.a.	n.a.	no

Foot-notes: ^a per year; ^b per harvested crop; ^c two-year rotation; ^d two harvest per year each averaging 160 bushel/acre; ^e one harvest per year; ^f six-year rotation; ^g seven-year rotation; ^h [10]; ⁱ [11]; ^j [12]; ^k [13]; ^l [14]; ^m [15]; ⁿ[16]; ^o [17]; ^p no irrigation for tree crops, no fertilization beyond initial seedling establishment

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Nomenclature

Acronyms

a.r.	as received
AD	anaerobic digestion
ASU	air separation unit
BFB	bubbling fluidized bed
BFBG	bubbling fluidized bed gasifier
BIGCC	biomass integrated gasification combined cycle
cf.	refer to
CFBG	circulating fluidized bed gasifier
CH ₄	methane
CHP	combined heat and power
CO ₂	carbon dioxide
COD	chemical oxygen demand
DDG	dried distillers grain
DDGS	dried distillers grain with solubles
DOE	department of energy
Eff _{G-FB}	gross thermal efficiency fuel-based = (energy in bio-oil + useful energy products) / energy in biomass
Eff _{G-PB}	gross thermal efficiency process-based = (energy in bio-oil + useful energy products) / (energy in biomass + auxiliary energy input)
Eff _{N-FB}	net thermal efficiency fuel-based = energy in bio-oil / energy in biomass
Eff _{N-PB}	net thermal efficiency process-based = energy in bio-oil / (energy in biomass + auxiliary energy input)
EFG-FT	entrained flow gasification and Fischer-Tropsch synthesis
ESP	electrostatic precipitator
EtOH	ethanol
FAEE	fatty acid ethyl ester
FAME	fatty acid methyl ester
FB-comb.	fluidized bed combustion
FCC	fluid catalytic cracking
FT	Fischer-Tropsch
FTS	Fischer-Tropsch synthesis
GGE	gallon gasoline equivalent

GHG	greenhouse gas
GIS	geographic information system
GTL	gas-to-liquid
H	mass fraction of hydrogen in the fuel on a dry basis
HHV	higher heating value
HT	high temperature
IEA	international energy agency
IGCC	integrated gasification combined cycle
LCA	life cycle analysis
LHV	low heating value
LPG	liquefied petroleum gas
LSFO	low sulfur fuel oil
LT	low temperature
M	module, an integrated block that contains multiple unit operations
M. C.	moisture content in wt%
M_{db}	moisture content on a dry basis
MGY	million gallons per year
MSW	municipal solid waste
M\$	million U.S.\$
M_{wb}	moisture content of the fuel on a wet basis
NPK	fertilizer nutrients: nitrogen, phosphorous, and potassium
OLR	organic loading rate
PM	particulate matter
PSA	pressure swing adsorption
PTE	process thermal efficiency
RCCOND	rankine cycle with condensing steam turbine
RT	residence time
SNG	synthetic natural gas
TCOD	total chemical oxygen demand
TOP	combined torrefaction and pelletization
U	unit operation, a basic step in a chemical engineering process
w.r.t.	with respect to
WGS	water gas shift
y	per year (365 days)
λ	latent heat of vaporization of water (2.31 MJ/kg at 25°C, constant volume)

Units

\$	US dollar
°C	degree Celsius
bar	100,000 Pa
BBL	barrel crude oil, 42 gal
cm	centimeter
C	capital investment
cal	calorie
CF	cubic foot, 28.3 L
cP	centi Poise, 0.001 Pa·s
g	gram
G	giga
gal	US gallon
GWh	giga Watt hour
h	hour
kg	kilogram
kW	kilo Watt
kWh	kilo Watt hour
L	liter or dm ³
M	mega
m ³	cubic meter
MCF	mega-cubic feet
mg	milligram
Mg	megagram, tonne
MJ	mega Joule
mm	millimeter
MWe	mega Watt of electricity
MWth	mega Watt of thermal
Pa	Pascal
ppm	parts per million
S	scaling factor
s	seconds
ST	short ton, 1 ST= 907 kg
t/d	tonne per day
tonne, t	1,000 kg
V	volume

Subscripts

e, el electric
th thermal

1. Introduction

1.1 The Biorefinery Concept

The term “biorefinery” was established in the 1990s [18], and was defined in the International Energy Agency (IEA) Biorefinery Task 42 [19] as:

“Biorefinery is the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)”

and in the U.S Department of Energy (DOE) Biomass Program [20] as:

“(Biorefinery systems are) similar to conventional refineries in that they produce a range of products to optimize both the use of the feedstock and production economics”

Both definitions clearly indicate that a biorefinery is a process where biomass is used as a feedstock and converted into affordable and sustainable bio-fuels, bio-power, and other bio-products.

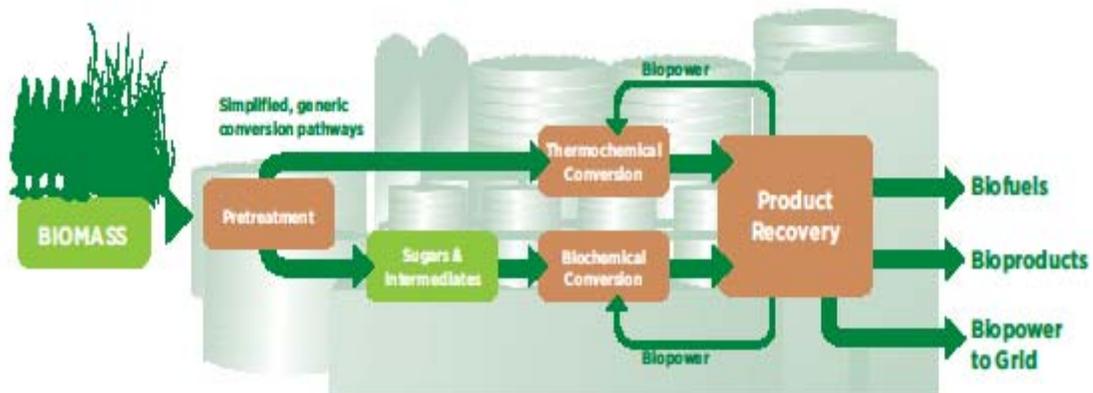


Figure 1.1. Integrated biorefinery using various conversion pathways [20]

As shown in the simplified schematic in Figure 1.1, a biorefinery can integrate biochemical and thermochemical conversion technologies to produce biofuels. Currently, biorefinery processes are in various stages of development worldwide (see Table 3.3).

With dwindling natural resources, increasing world population and a rising demand for fuel and electricity, there has been renewed interest in, and financial incentives for, renewable resources over the last 15 years. Accordingly, the number of pathways to arrive at desired products (fuels, chemicals, and electricity) is plentiful as illustrated by Figure 1.2. However, not all technological pathways are commercially available or viable for an island state such as Hawaii. This report assesses the current state of biorefinery component technologies and

(1) establishes baseline material and energy balances for well defined feedstock production and/or conversion modules;

(2) integrates the modules to investigate their use as components of tropical biorefineries; and

(3) provides preliminary estimation of production costs for the primary product of each module.

Novel and emerging conversion techniques are often proprietary and published data is often lacking. Recognizing this limitation, the available technologies were assessed accordingly. Technologies were categorized into biochemical, chemical and thermochemical conversions as shown below:

- Biochemical ethanol conversions
 - Anaerobic digestion with combined heat and power generation
 - Sucrose platform (sugar cane)
 - Starch platform (corn and cassava)
 - Lignocellulosic platform (woody plant matter, e.g. banagrass)
- Chemical conversion
 - Biodiesel platform (terrestrial and aquatic oil producers)
- Thermochemical conversions
 - Torrefaction

- Pyrolysis for bio-oil or bio-char production
- Gasification for liquid fuels synthesis
- Combustion for heat and electricity

These biomass conversion technologies can be integrated to form a biorefinery. Figures 1.3, 1.4 and 1.5 depict process routes and module combinations for the three primary energy products which are fuel ethanol, electricity and transportation fuels such as gasoline, bio-diesel, and jet fuel,. The routes and platform technologies as well as their unit operations, modules and processes are defined below:

- Unit operation: a basic step in a process;
- Module: an integrated block which may contain multiple unit operations;
- Process: an integration of all necessary steps to produce the target products from biomass feedstock;
- Platform: a process based on a specific feedstock or primary conversion technology;
- Route: a conversion pathway to a certain target energy product.

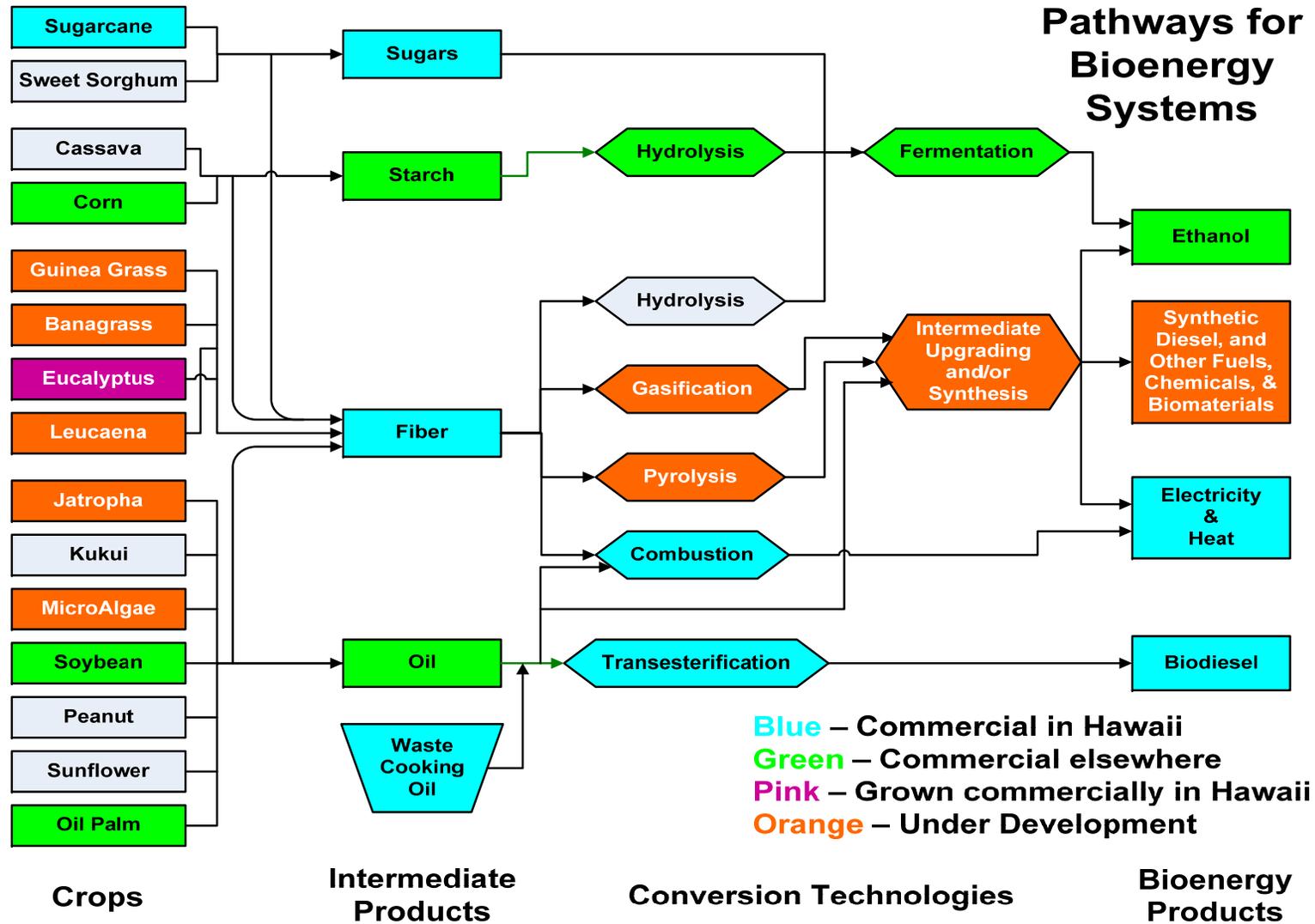


Figure 1.2. Pathways for bioenergy production systems [21]

Target product 1: electricity

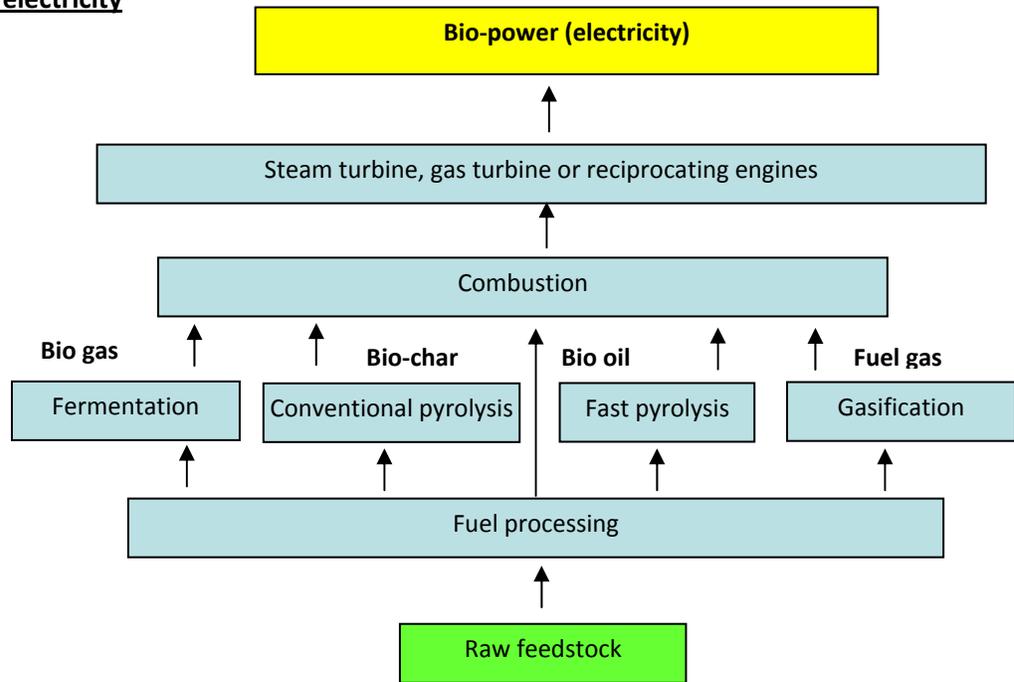


Figure 1.3. Diagram depicting seven modules and five routes to arrive at the target product electricity

Target product 2: transportation fuels

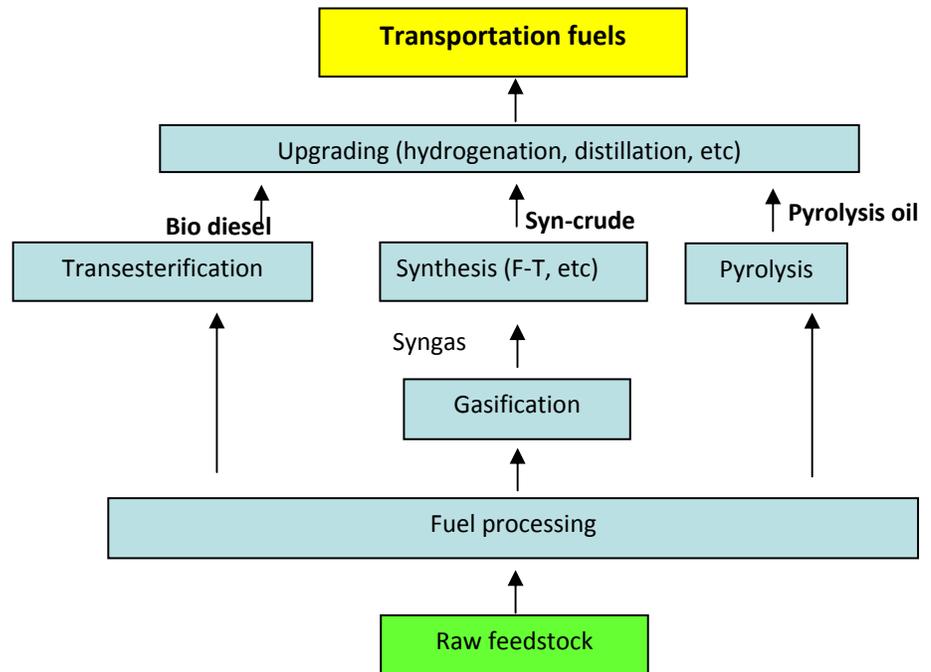


Figure 1.4. Diagram depicting six modules and three routes to arrive at the target product transportation fuel

Target product 3: fuel ethanol

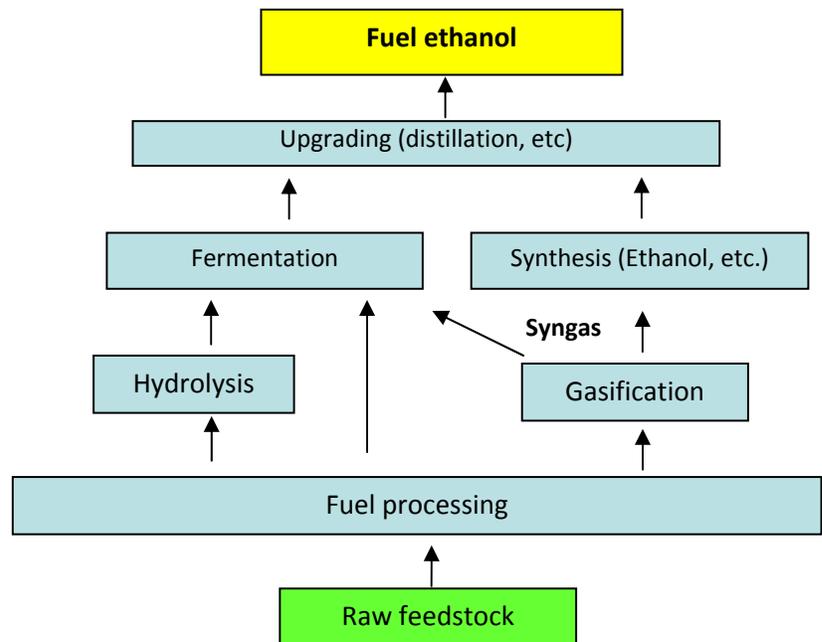


Figure 1.5. Diagram depicting six modules and four routes to arrive at the target product fuel ethanol

1.2 Energy Crops and Production Technology

Hawaii is known for its tropical climate with moderate temperature swings due to the near constant trade winds. However, precipitation and cloud cover can vary greatly due to topology. Generally, the windward side of higher mountains receives the majority of rain whereas the leeward side is characterized by a drier and sunnier climate. These variations have a significant effect on the type and yield of energy crops that can be grown.

The selected energy crops have been chosen with respect to yield potential, suitability for tropical climates and their potential to disrupt local ecosystems. With the exception of corn, each crop description has been replicated from [21].

Sugarcane

Sugarcane (*Saccharum officinarum*) originated in the southern Pacific region, most likely New Guinea. It grows well in the tropics where temperatures are warm, with moderately high rainfall, and heavy soils. Sugarcane has been grown commercially in Hawaii for more than 170 years and the technology for producing and processing sugarcane is well established in the state.

Soil preparation for sugarcane in Hawaii typically consists of leveling, as necessary; cross-ripping and dragging; multiple passes with large disc harrows; followed by rip-dragging the entire field. Sugarcane seed pieces, vegetative cuttings of young sugarcane stalks, are planted in furrows at a density of roughly 7 tonnes per hectare, using mechanical planters. Fertilizer (N, P, and K) can be applied at the time of planting or shortly thereafter.

Fertilizer requirements for sugarcane are relatively high with approximately 150 kg of nitrogen and potassium per hectare and 50-300 kg of phosphorous per hectare [22]. These can be applied initially with the planter as solid fertilizers or thereafter via the irrigation system.

Weeds can usually be kept under control with an effective weed control program. Weed control measures for sugarcane might include a pre-emergence herbicide, inter-row herbicide applications and spot applications as needed. Canopy closure occurs within eight weeks of

planting (slightly longer during the winter), after which in-field weed control becomes unnecessary. Considerably less weed control is required for ratoon (unseeded regrowth following harvesting) crops owing to heavy ground cover from harvesting operations and rapid canopy closure following harvesting.

For optimal growth, sugarcane needs ~180 cm (70 inches) of irrigation (via rainfall or applied mechanically) per year. If rainfall is not adequate, sugarcane is irrigated through drip irrigation.

Commercially grown sugarcane in Hawaii is normally ripened through a combination of water withdrawal and the application of a chemical ripener toward the end of its growth cycle in order to maximize the sucrose content. Typically, the field is burned immediately before harvesting to reduce the amount of extraneous fibrous material (called “sugarcane trash”).

Throughout most of the cane-growing world, the plant crop (i.e., the seeded crop) for sugarcane is harvested at 14 to 18 months of age, then, annually, in ratoon crops. By contrast, sugarcane grown commercially in Hawaii is harvested, nominally, at 24 months intervals. In Hawaii, sugarcane typically is harvested using push rakes (V-cutters and other mechanical harvesters also have been used in the past). The reaped cane is consolidated into large windrows in the field, and loaded into truck-trailers using hydraulic cranes. The truck-trailers carry loads of 20-50 tonnes of cane to the sugar mill.

Most sugarcane producers have owned and maintained large networks of private agricultural roads including a broad, paved, cane-haul system that interconnect all fields with the sugar mill. This road network provides adequate infrastructure to transport harvested sugarcane from the field to any processing facility.

Technology Gaps

Because sugarcane has been produce commercially in Hawaii for nearly two centuries, there are no major technology gaps in the production, harvesting, and delivery of sugarcane, though refinements potentially could increase yields and reduce costs incrementally. Whether sugarcane produced in Hawaii should be grown under a one- or two-year cycle and whether sugarcane grown for energy purposes should or should not be burned prior to harvesting, continues to be

debated. Decisions on such questions would impact agronomic, harvesting and transporting practices as well as the breeding and selection of commercial sugarcane varieties.

Banagrass

Bana or Elephant grass (*Pennisetum purpureum Schumach*) is of tropical African origin but has been introduced to most tropical areas of the world and has become naturalized throughout Southeast Asia. It typically grows as a perennial in tropical areas of South America and Asia. Banagrass is not being produced commercially in Hawaii at this time, though cultivars of banagrass have been grown in the islands for use as windbreak and on trial bases as energy and forage crops. Banagrass grows on a wide range of soil types, best in deep, well-drained friable loams with a pH of 4.5-8.2. Banagrass grows best in temperatures between 25 and 40°C, and shows little growth below 15°C [21].

Though not fully optimized for commercial production, cultivation and harvesting strategies have been developed for banagrass grown as an energy crop and ongoing research is being conducted on this species at the University of Hawaii at Manoa. Owing to similarities between banagrass and sugarcane, production strategies often mimic those for sugarcane, with a few exceptions, as noted below.

Soil preparation would be very similar to that used in sugarcane. The planting density of banagrass seed pieces would be considerably lower than for sugarcane, around 2 to 3 tonnes per hectare. Fertilizer application and irrigation are comparable to sugarcane both in rate and method of application. Banagrass is listed as an invasive species in the Pacific Islands and in Florida; though it can be controlled by regular cutting or by applying herbicide. A recent study of banagrass in Hawaii concluded that banagrass has not become an invasive pest and it does not show signs of becoming a serious invader in Hawaii [23].

It is anticipated that banagrass can be harvested at eight months of age, though trials being performed by the University of Hawaii at Manoa are investigating shorter rotation cycles. The harvesting schedule would have to be adjusted to avoid flowering (terminal growth of banagrass and sugarcane ceases once flowering occurs), which takes place during the winter and early

spring in stands exceeding four months of age. Two types of systems for harvesting and transporting banagrass have been tested in Hawaii: (1) sugarcane billet harvesting systems and (2) forage harvesting systems. The billet harvesting system has been tried on a fairly large scale, approaching 400 hectares, at the former Waialua Sugar Company on Oahu, more than a decade ago. Both billet sugarcane harvesters and forage harvesters are commercial but their application to Hawaiian conditions would require additional evaluation to determine the best set of technology options to serve both crop production (adaptability to terrain, field efficiency, harvesting throughput, etc.) and conversion facility (feedstock particle size, moisture content, etc.) requirements. It is anticipated that banagrass would be ratooned multiple times before being replanted.

Technology Gaps

Most of the procedures presently used for growing and harvesting banagrass have been extrapolated from sugarcane production and have not been optimized for banagrass. Major technology gaps for banagrass include breeding and selecting superior cultivars, establishing crop management practices specifically tailored to banagrass, and developing better harvest and transport systems.

Eucalyptus

Eucalyptus trees, originally from Australia, were brought to Hawaii as a prospect for commercial timber production. Various species have been introduced into the state and can be found on the major inhabited islands. *Eucalyptus* generally prefers temperate to tropical regions with sufficient rainfall that is distributed throughout the year. There are possibly 600 species of *Eucalyptus* worldwide; more than 90 (not including ornamental species) have been planted in Hawaii. The most commonly planted species in Hawaii are *E. botryoides*, *E. camaldulensis*, *E. citriodora*, *E. deglupta*, *E. globulus*, *E. grandis*, *E. microcorys*, *E. paniculata*, *E. pilularis*, *E. resinifera*, *E. robusta*, *E. saligna*, and *E. sideroxylon*.

The most productive species grow best in areas of moderate to high rainfall (>110 cm). Other species grow well on lands having as little as 50 cm (20 inches) of rainfall. Typically, *Eucalyptus*

is not irrigated, rather, species are selected to match rainfall at the particular location. Some species are adapted to warm temperate regions and in Hawaii grow at elevations of up to 2000 meters. Above this altitude, moisture becomes severely limiting. The most productive sites in Hawaii are below 1000 meters elevation. The potential for *Eucalyptus sp.* to be invasive in Hawaii was recently assessed [23]. Findings indicate that maintaining buffers between production areas and waterway and wetlands and annual monitoring programs could help reduce *E. grandis* invasion risks.

If trees are planted on abandoned sugar cane land, heavy rollers are used to cut and crush cane and other vegetation. If the area is covered with very heavy vegetation or brush, a tractor equipped with a bulldozer blade could be used. The blade is held above the ground to knock down heavy brush so that a harrow or roller can crush the material. On some lands, a tractor equipped with wide-gauge shoes can be used to pull a heavy-duty, off-set cutaway harrow. After clearing, herbicide spray can be applied if the vegetation returns before planting. Tree seedlings are planted about two weeks after herbicide spraying.

Young trees do not compete well with weeds, especially in fertile soils. The critical period of development is two to three months after planting, when regrowth of a previous crop or weeds compete with the tree seedlings. Weeds should be kept under control with one application of herbicide prior to planting and two or three applications following planting. Post-planting weed control is performed with manual backpack sprayers or using tractor-mounted sprayers. At the early stage, trees are sensitive to herbicide so care should be taken to avoid contact between the herbicide and the young plants.

Tests have shown that *Eucalyptus* responds well to fertilization, particularly to nitrogen. *Eucalyptus* grown on oxisols has shown phosphorus deficiency. Intercropping *Eucalyptus* with the nitrogen-fixing legume *Falcataria moluccana* (common name albizia) greatly improved growth and production of the *Eucalyptus* over chemically fertilized trees on the Hamakua coast.

Optimal harvesting age varies with species and environments, but is normally performed around seven or eight years of age. The harvesting operation for trees is fully mechanized using commercially available equipment. A feller buncher unit, capable of cutting 0.35 m diameter

stems, could be used to harvest standing trees. In this system, stems are sheared at the base using hydraulic shears located at the base of the feller buncher. Clean shearing would be required to minimize stump damage for good coppice regrowth. Most production scenarios, however, favor replanting over coppicing. Following tree felling, skidder/forwarders collect the felled trees and transport them as logs, to hauling units or to centralized in-field locations where the trees would be chipped.

Technology Gaps

As noted above, a large number of *Eucalyptus* species have been planted in Hawaii. There is opportunity for yield improvement through better selection of species for particular environments. The most significant technology gap associated with *Eucalyptus* involves selecting appropriate harvesting and transporting systems that are well suited to Hawaii's challenging terrain and other conditions.

Leucaena

Leucaena (*Leucaena leucocephala*) is a nitrogen-fixing tree or shrub, originating in Mexico and Central America. It was introduced to Hawaii as fodder. "Giant" *Leucaena* is a tree form that shares many of the traits of the more common forms of *L. leucocephala*, but does not seed and has larger stems. *Leucaena* is a drought tolerant species and is usually found in lower elevations in locations with lower rainfall. *Leucaena* grows well in neutral or slightly acid soils, and does poorly in very acid soils. With proper management, the giant *Leucaena* tree grows at a rapid pace from transplanting to mature height, growing roughly one meter per month during the first five months and reaches a height of greater than 15 meter after six years of growth. The University of Hawaii at Manoa continues to perform research on this crop.

Fertilizer application is limited to planting as the tree is nitrogen fixing. Giant *Leucaena* can be established directly from sown seeds or from transplanted, 3 to 4 month old seedlings. As an energy crop, this plant species would most likely be grown from transplants. It is anticipated that ~10,000 trees per hectare would be optimal for an energy plantation.

When cut down, the tree can produce a cluster of branches up to 10 meters in length within one year. However, if planted in a dense stand and harvested regularly, it can be maintained for decades as a low shrub.

Brewbaker [24] considered five alternative harvesting and transporting systems for giant *Leucaena*. The swathe-felling mobile chipper was proposed as the best methods for harvesting *L. leucocephala* in Hawaii because it is capable of felling trees and chipping them directly in the field with minimal manpower. Other mechanized harvesters like feller bunchers, grapple skidders and roadside chippers require more skilled operators and are better suited to larger trees planted at lower densities.

Technology Gaps

Technology gaps in *Leucaena* production are similar to Eucalyptus. However, because *Leucaena* has not been produced in large quantities in Hawaii, in addition to selecting appropriate harvesting and transporting systems, additional research would be needed to optimize crop management practices. A recent study of invasiveness of candidate biofuel crops in Hawaii [23] found that arboreal varieties of *Leucaena* were spreading from their planted locations and spread distances were substantial, i.e. at least 300 m. Control of invasiveness should be considered an additional technology gap.

Jatropha

Jatropha (*Jatropha curcas* L.) most likely originated in the Mexico - Central America region. It is known in English as Barbados nut, castor oil, Chinese castor oil, curcas, fig nut, physic nut, pig nut, purging nut, and wild oil nut. This perennial monoecious species is a shrub or small tree (6 m) with spreading branches. It has been spread world-wide as a medicinal plant into tropical regions. The plant readily establishes itself and is regarded as an invasive weed in a number of countries. A recent assessment of invasiveness of *Jatropha* plantings in Hawaii found that plants have spread beyond their planted locations, particularly in areas near waterway or on sloped ground.

Jatropha nuts are high in protein and fat; however, they contain an albumin poison, toxalbumen cursin, and a toxin, curcasin, which makes eating them potentially fatal. There has been much interest in non-toxic varieties of *Jatropha* that, potentially, could provide byproducts, such as animal feed, which could make the economics of *Jatropha* production and conversion into biofuels more attractive.

The succulent species can be found in locations ranging from dry tropic to moist subtropical to wet tropical forests. It grows best in temperatures ranging from 20 to 28°C, and can be found from sea level to 1500 m elevation. Its adaptability to drier tropical climates and poorer soils makes this oil bearing species an attractive energy crop for application to marginal agricultural lands in Hawaii.

The tree can be propagated from cuttings and seeds. The cuttings root readily. Seeds germinate in about 10 days. The best time to start in the field is at the beginning of the rainy season. The young plant is sensitive to weed competition during establishment, although, normally, tillage is not needed (only the area around the plants needs to be cleaned). Plant spacing of 2 m x 2 m, 2.5 m x 2.5 m, and 3 m x 3 m have been recommended. The plant should be hedged and pruned to maintain its shape and has a productive life of 40 to 50 years. As a hedge, the planting distances should range from 15 to 25 cm.

The *Jatropha* plant produces a fruit measuring about 3 cm in diameter that contains an oil bearing kernel. In developing countries, the fruit is harvested by hand, but mechanical harvesting would be required in any commercial operation in Hawaii. At present, *Jatropha*'s flowering is not synchronized. This results in fruit at various stages of maturity being present on the plant at any given time. Methods to address asynchronous flowering could include plant breeding, cultural practices, or selective harvesting. The latter would require development of harvesting equipment that removes only ripe fruit and does not disturb immature fruit and flowers. Given that the oil bearing kernel is only a small fraction of the mature fruit weight, the harvesting equipment might also remove the kernel and return the fruit pulp to the field surface as mulch. Use of the fruit pulp as a byproduct could justify whole fruit harvesting. Modified mechanical harvesting equipment for blueberries and olives have been proposed for *Jatropha* harvesting, however, to date, no performance test data has been published.

Technology Gaps

Jatropha presently is in the R&D stage of development in Hawaii. Superior varieties need to be identified and sound management practices have yet to be developed. The availability of non-toxic varieties of *Jatropha* could improve the economics of biofuel production by providing a seed meal that is rich in protein, which could be used to generate an animal feed byproduct. Mechanical harvesting systems need to be developed.

Corn

Although corn is best known worldwide from USA Corn-Belt hybrids, it is actually a tropical plant. It has taken a century of breeding to make corn well-adapted and productive in the temperate climates [15]. The most widely used corn for ethanol production is the yellow dent corn, also known as commodity or field corn. However, the development of corn-to-ethanol facilities in Hawaii would be contingent on the use of tropical hybrids resistant to tropical diseases such as the Maize Mosaic Virus, Southern Rust, Turcicum blight, etc. Most Hawaii-bred hybrids can be grown without using pesticides [25].

Corn matures rapidly in the tropics. On Hawaii's prime agricultural land, sweet corn, green shop (silage corn) and field corn (dry grain) ripen in 70, 95 and 110 days, respectively [25]. Although in Hawaii corn can be grown throughout the year, yields can vary significantly from month to month. Typically, summer month yield about twice as much corn compared to winter corn [25]. Brewkaker [25] summarized field trials on Oahu (Waimanalo) as follows: "Monthly plot plantings for four years at Waimanalo averaged 155 bushels per crop acre of grain, or 472 bushels per acre per year. Outstanding hybrids (H1015, H1035) showed an average yield of 175 bus/A per crop, and regularly exceed 200 bus/acre in summer trials without fungicides or insecticides." However, considering the negative effects of continuous corn cropping on soil quality and pest control, it seems favorable to interrupt corn cropping in the winter by planting a nitrogen fixating cover crop such as clover. Consequently, only two dry grain harvests per year would be possible, yielding a more conservative estimate of about 320 bushel per acre per year (underlying assumption for corn-to-ethanol conversion in this report).

Cassava

Cassava (*Manihot esculena*) is a starch-rich feedstock and is primarily grown in a tropical climate. Although originally from the Amazon region of Central America, it is widely grown in South East Asia and Africa as a food commodity. The plant is also known by different names such as Yuca, Manioc, Mandioca, Maniok or Tapioca. Cassava can be grown in all-types of soils. Ideally sandy loam and loamy sand soils provide excellent conditions for cassava rootformation. Importantly, it can be cultivated on lands where other crops cannot be grown economically [15]. The major cassava producing nations are Nigeria, Brazil, Thailand, Indonesia and Congo. The world Cassava production was nearly 218 million tons in year 2006.

Cassava contains relatively low protein and other nutrients. Thus it could serve as an ideal feedstock for ethanol production. Additionally, it can be grown in otherwise infertile land with minimal input of chemicals, such as fertilizers, herbicides and insecticides, making it one of the cheapest agro-based feedstocks [15].

The cassava yield shows a considerable variation depending on several factors including soil types, nutrient and water availability. In this report, an average fresh tuber yield of 20 t/acre and a starch content of 25% is assumed, although higher yields of up to 35 t/acre have been reported [15].

Technology Gaps

The harvesting is done manually and requires cheap labor. Therefore, cassava is primarily grown in developing countries, where the labor supplies are abundant at a reasonably low cost. A mechanized harvesting system similar to potato harvesting can be used with some modification [15].

Microalgae

Microalgae typically are unicellular aquatic organisms, although some can form chains. These organisms function as nutrient recyclers and lie at the base of many food chains in aquatic ecosystems. The aquaculture industry relies extensively on such autotrophic microorganisms as live feed for commercially valuable filter feeding organisms such as shrimp and clams.

Presently, considerable research on microalgae is being conducted by private industry, universities and government research laboratories. The University of Hawaii at Manoa has a number of active projects in this area.

Various growth chambers, or photobioreactors, have been tested and used in culturing microalgae. Production systems differ by the manner in which nutrients, cells and light are introduced into the system.

Open production systems are exposed to the ambient environment; closed systems have barriers aimed, in part, at preventing contamination. Open systems typically cost less to operate and maintain than closed systems. However, outdoor algae production systems are more susceptible to the introduction of undesired algae species and other contaminants. Open systems have been used commercially mainly for algal strains that grow in very harsh environments, such as high salinity or extreme pH, which reduces the likelihood of contamination by other undesirable aquatic organisms.

Ponds are sometimes used for mass cultivation of algae. There are three common algal pond designs, each having its own method for mixing the algae: (1) Circular ponds with mechanical arms or air bubbles for mixing; (2) Raceways with paddle wheels; (3) Sloped raceway type ponds with a circulating pump. Closed photobioreactors are being used commercially to produce microalgae for nutraceutical applications, though commercial closed systems generally have been quite small in scale. Cellana and Cyanotech have successfully produced microalgae in large closed photobioreactors in Kailua-Kona on Hawaii island, though production costs are believed to be far too high for producing microalgae targeted to the energy market. Other contenders employing the closed systems include Algenol and Solazyme. Algenol uses a genetically modified strain of cyanobacteria capable of converting photosynthetically produced starches into ethanol. Ethanol then diffuses out of the cells into the surrounding broth, where it can be separated by distillation. Solazyme on the other hand uses algae to produce lipids from a sugary substrate in a heterotrophic reaction analogous to conventional fermentations.

Microalgae production systems are normally classified as batch, semi-continuous, or continuous, depending on how often cells are removed from the system and how nutrients and carbon

dioxide are added to enhance growth rate. A batch system requires harvesting all algae from the system once a desired cell density is reached. Batch systems are considered the most reliable because the cultures are not kept longer than necessary to produce the desired cell density or product characteristic. Semi-continuous cultures are partially harvested after the desired cell density is obtained. The desired combination of nutrients and cells can then be added for the next growth cycle. Harvesting and replenishing nutrients occurs continuously in a continuous system. In principle, continuous systems can be more efficient and provide a higher rate of production over time than batch or semi-continuous systems. However, maintaining cell densities and nutrients at target levels can be complex and costly.

As with the terrestrial energy crops described above, harvesting efficiency has a major impact on the economics of microalgae. Harvesting microalgae is costly because: (1) individual cells normally vary widely in size; (2) algae cells have low specific gravity, making them difficult to settle quickly; (3) algae broth is very dilute, often below 20 g/L. Various harvesting techniques have been proposed and include sedimentation, flocculation, centrifugation, and foam fractionation.

Sedimentation has been used for separating larger sized particles (>100 μm). Settling times for smaller agglomerates are impractical so that flocculants must be used. However, flocculants can change the chemical properties of algae, which could be problematic for certain end uses. Centrifugation is a reliable technique for extracting algae from the growth medium, though centrifuges are costly and consume considerable power. Foam fractionation is an adsorptive bubble separation technique that selectively transfers microscopic particles and dissolved materials from liquid cultures to flowing gas bubbles that gather at the air-liquid interface and can then be removed. Foam fractionation has been tested in Hawaii and has been shown to be a promising technique to facilitate the harvesting of microalgae.

Technology Gaps

There are enormous technology gaps in algae production. These include developing (1) improved strains of algae that do not present invasive species risks, (2) large photobioreactors that allow for efficient penetration of sunlight, (3) more effective methods to distribute carbon

dioxide and nutrients in water, and (4) better and more energy-efficient methods to harvest and separate microalgae from water.

1.2 The Scope of Report

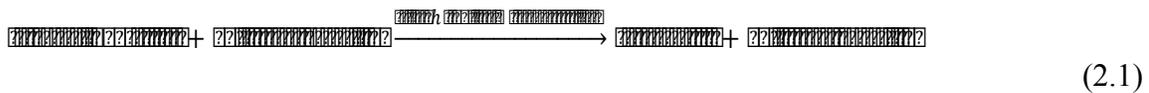
The Hawaii Natural Energy Institute [26] has been involved in biomass energy research and development for many years. Recently, new interest and research was spurred by the Hawaii Clean Energy Initiative (HCEI), which outlined a roadmap that moves Hawaii from a 90 percent dependence on imported fossil fuels into a future, where 70 percent of its electricity and ground transportation fuels will come from renewable sources by the year 2030. As part of this effort, HNEI provides this report that analyses and evaluates future commercial bio-refineries based on their potential output of biofuels and electricity, their cost and natural resource demands and their proximity to commercial realization.

Based on the availability of biomass resources in the state and currently available technologies, biorefinery strategies to produce fuels and electricity are described in this report. Each processing route contains one or more platform technologies which are based on the feedstock and the configuration of the process. A general process description is provided for each platform technology as well as an energetic yield analysis and capital cost evaluation. For convenience, each platform technology is reduced to a block diagram with major input and output streams depicted. In summary, the platform technologies are evaluated using three scale scenarios for a biorefinery and various feedstocks.

2. Biorefinery Technologies

2.1 Biochemical Conversion Platform

Biochemical conversions of organic material to value-added products (e.g. fuels) involve the use of microorganism as biocatalysts. The reaction is usually referred to as fermentation, and is often described as autocatalytic since the consumption of feedstock results in the formation of products and further microorganism as illustrated in the following equation:



Sugars are the most common form of feedstock, whereas organic acids, alcohols, carbon dioxide, water and hydrogen are typical end products. Generally, fermentations can be performed with (aerobic) or without (anaerobic) the presence of oxygen. Lack of oxygen usually leads to the donation of electrons from the substrate to an organic compound (e.g. ethanol) through a series of electron transport events, whereas aerobic fermentations often completely oxidize the substrate to carbon dioxide and water. The inherent differences in metabolic pathways between aerobic and anaerobic metabolism is responsible for their different outcomes. That is, aerobic fermentations yield a maximum of Adenosine triphosphate (ATP), which is typically used for cell growth, whereas anaerobic pathways contribute to the formation of reduced organic compounds (e.g. organic fuels).

Table 2.1 illustrates the benefits and drawbacks of various potential biofuels or biofuel-precursors (organic acids), which can be produced through fermentation and why ethanol, as of today, is the favored fuel. Today's popularity of biochemically-derived ethanol can be explained by its ease of recovery due to high product titers, high volumetric productivity to low capital cost ratio, and years of experience producing this product in commercial-scale facilities. Methane fermentations are slow, however they are capable of utilizing a broad spectrum of none-sterile substrates such as plant sugars, proteins, fats, water-soluble lignin and other organic compounds. Furthermore, product recovery is a trivial gas/liquid separation. Unfortunately, methane's volumetric energy density at standard conditions is extremely low (about 1/1000th that of

gasoline) such that liquefaction or compression would be necessary to use this gas as a transportation fuel. However, the methane is often used on-site for electricity/process heat generation or for feed-in solutions. Butanol fermentations still exhibit a considerable technological gap with regard to energy efficient recovery methods, and are therefore at this point, not considered in this report.

Table 2.1. Various biochemical conversions and their characteristics

Product	Substrate	Final product titer [27]	Productivity [27] g/L/h	Scale realized	Energy content compared to gasoline at STP	Recovery /energy intensity
Ethanol	Plant sugars	130 g/L	3-5	Commercial	66%	Distillation /moderate
1-Butanol	Plant sugars	20 g/L	0.5	Pilot	90%	Distillation /high
n-Butanol	Plant sugars	n.a.	n.a.	Pilot	90%	Distillation /high
Methane	Plant sugars, fats, proteins	50-70% (waste water handbook)	0.01-0.05	Commercial	0.1% (1atm, 20°C)	Gas-liquid separation /very low
Organic acids (e.g. citrate, lactate)	Plant sugars	50-150 g/L	0.5-2	Commercial	50% (lactic acid)	Esterification+ distillation /moderate

Baker's yeast, *Saccharomyces cerevisiae*, is the most commonly used microbe to produce ethanol from sucrose, starch or lignocellulosic biomass. Because the metabolic pathways of yeast requires the presence of simple sugars (glucose, fructose, galactose, sorbose, sucrose), feedstocks containing mostly starch (e.g. corn, cassava, potato) or cellulose (fibrous plant material such as wood chips, grasses etc.) need to undergo a pretreatment process before fermentation can occur. Therefore, based on the nature of the feedstocks, three types of ethanol platforms can be distinguished: sucrose, starch, and lignocellulosic ethanol refineries. A fourth platform has recently been identified in which synthesis gas (carbon monoxide and hydrogen) is used in a biochemical reaction to produce ethanol and acetic acid. Due to the novelty of the process and limited amounts of reliable and accessible data, this avenue will not be explored at this time.

2.1.1 Anaerobic Digestion and CHP Platform

Anaerobic digestion is the process of microbial breakdown of complex organic compounds such as sugars, fats and proteins under the exclusion of oxygen. Final metabolites include methane, carbon dioxide, hydrogen and stabilized volatile organic matter (see Table 2.2). Although anaerobic digestion of degradable waste streams that are common and abundant in today's ethanol producing facilities offers many benefits (see above), it has not been adapted at the magnitude possible [28].

Table 2.2. Typical composition of biogas from an anaerobic digester [29]

Methane (CH ₄)	55-65 %
Carbon dioxide (CO ₂)	30-40 %
Hydrogen (H ₂)	1-2%
Hydrogen sulfide (H ₂ S)	30-150 ppm
Other gases	1-2 %

Anaerobic digestion has often been cited as an effective and economical treatment option for waste streams that are high in TCOD (Total Chemical Oxygen Demand) [28, 30]. Since ethanol production from biomass through fermentation generates an undesirable amount of liquid effluent high in TCOD and nutrients (stillage), anaerobic digestion can provide the means to reduce the organic load of the waste stream. Moreover, the resulting biogas is of high caloric value and can be burned to produce heat and power to supplement on-site energy demands. The liquid effluent of an anaerobic digester is low in odor and rich in plant nutrients and therefore amenable to irrigation and fertilization of cropland.

Process Description

Anaerobic digestion involves three groups of microbes: Liquefying bacteria, acidogenic bacteria and methanogenic bacteria. As their names suggest, liquefying bacteria turn complex carbohydrates into water-soluble sugars which, together with proteins and fats, are used as substrates for acidogenesis (organic acid formation). Finally, organic acids are converted to methane and carbon dioxide by methanogenic bacteria.

Based on the reactor temperature, three process regimes are commonly distinguished in anaerobic digestion: the psychrophilic (5-15°C), mesophilic (20-45°C, usually 37°C) and thermophilic (50-65°C, usually 55°C) temperature range. Psychrophilic digestion often occurs in natural processes such as on lake bottoms, whereas mesophilic and thermophilic digestion are most common in industrial settings. The hydraulic retention time for mesophilic processes is in the range of 15-30 days while thermophilic digestion only requires a residence time between 10-15 days [30].

Assumptions for digester and CHP performance

Table 2.3 compares digester performance from various researchers with regard to substrate, methane yield, productivity and temperature regime.

Table 2.3. Anaerobic treatment of various substrates (values are calculated from literature data)[30-32]

Substrate	Temperature regime	OLR (g COD/L/day)	Treatment efficiency (TCOD removed, %)	Methane yield (L/g TCOD)	Methane productivity (L/L/day)
Thin stillage from cane molasses	Mesophilic	12.25	71	0.26	3.84
	Thermophilic	23.5	61	0.17	3.37
Cellulosic (Eucalyptus)	Mesophilic	10.7	87	0.4	2.7
Thin stillage from dry mill corn ethanol	Mesophilic	2.2	79	0.27	0.47
	Thermophilic	7.5	90	0.25	3.4

Based on this data and taking into account that raw thin stillage has a temperature of 80-90°C as it exits the distillation process (little additional heating/cooling required), anaerobic digestion will be based on the following assumptions:

- Thermophilic temperature regime, heating requirements provided by hot thin stillage
- Organic loading rate of 7.5 g TCOD/L/day
- Treatment efficiency of 75% w.r.t. TCOD

- Methane yield of 0.25 m³/kg TCOD
- Methane productivity of 3 L/L/day

Due to the production of thin stillage as a waste stream in most bioethanol conversion processes, the concept of anaerobic digestion is incorporated into each biochemical conversion platform that is described in the next chapters.

Furthermore, all of the biochemical platform technologies (with the exception of sugar cane) have thermal and electrical power requirements that are typically provided by burning natural gas or coal and by importing electricity from the grid. However, using the produced methane from anaerobic digestion, a large part of the thermal energy and all of the electrical demand can be met through combined heat and power (CHP) generation. Typical conversion technology and performance data is listed in Table 2.4.

Table 2.4. Systems for cogeneration of heat and power (CHP) and their characteristics [15, 21]

	Reciprocating engine	Micro-turbine	Fuel cell
Typical unit size, kW	150 – 3,000	30-300	200
Electric efficiency, %	30-40	25-30	40-50
Thermal output/Fuel input, %	35-50	40-50	35-45
Typical capital cost, \$/kW	1,200-1,500	1,500-2,000	4,000-6,000

Based on this data, future electric and thermal conversion efficiencies in this report are assumed to be 30% and 50%, respectively (independent of technology). Consequently, as depicted in Figure 2.1, 250 L of methane (HHV_{CH₄}=36.4 MJ/m³) will generate 2.7 MJ (0.75 kWh) electricity and 4.5 MJ of thermal energy.

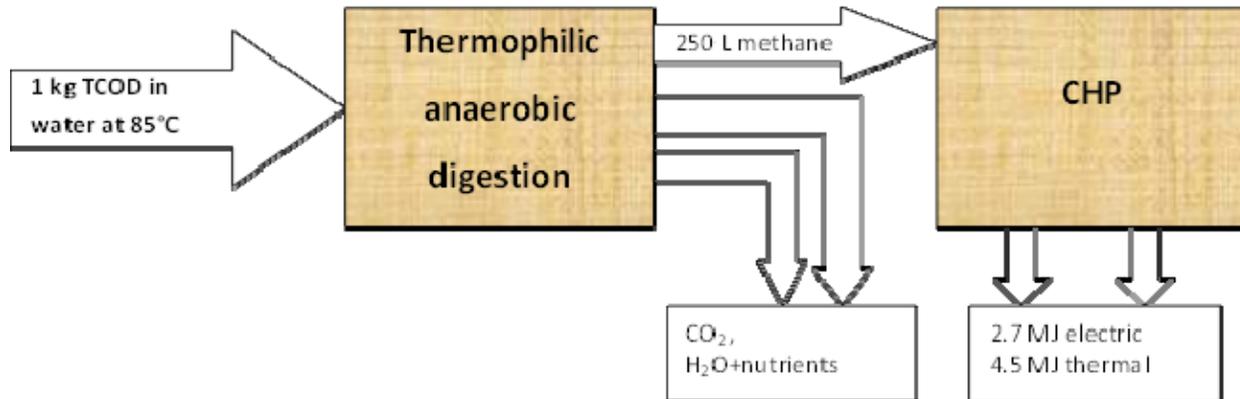


Figure 2.1. Block flow diagram of the anaerobic digestion and CHP platform

Capital cost of anaerobic digestion and CHP

Due to the increasing popularity of small to medium size onsite anaerobic digestion and CHP systems, there is a growing selection of “off-the-shelf” commercial turnkey systems available. Wilkinson [33] estimated the cost of a typical 500 kW_{el} biogas plant to be about 3,500 Euro/kW_{el} using data from 2006. Assuming an exchange rate of 1.3 Euro/\$ and accounting for economy of scale with an estimated scaling factor of S=0.7, the total investment cost of biogas plants can be estimated through the following equation

$$\frac{C_1}{C_2} = \left(\frac{Q_1}{Q_2}\right)^S \quad (2.2)$$

where C is the capital investment and Q is the plant output. If electric output is correlated with TCOD using data presented in Figure 2.1, the following graph can be established (Figure 2.2):

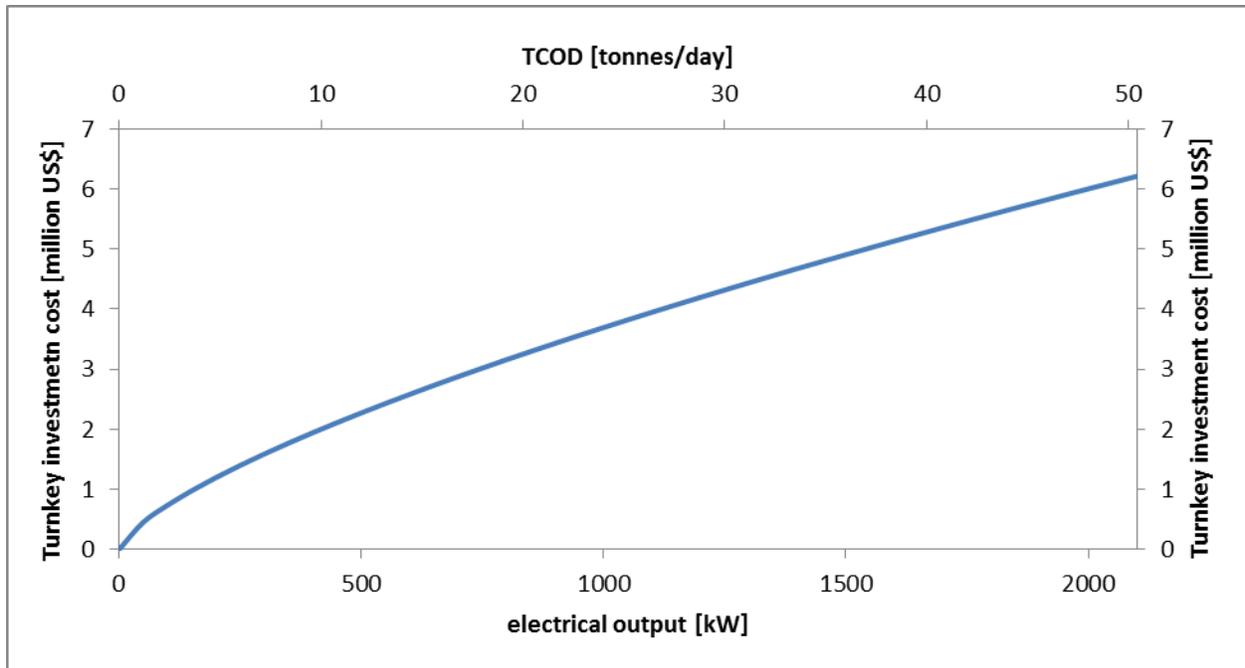


Figure 2.2. Turnkey investment cost of an AD-CHP plant based on data from [33], an exchange rate of 1.3 Euro/\$ and a scaling factor of $S=0.7$

2.1.2 Sucrose Platform

Sucrose is a disaccharide that is formed when a glucose and fructose molecule undergo a condensation reaction and is commonly referred to as table sugar. Sugarcane and sugar beets are the two primary crops farmed in tropical and temperate regions, respectively, for sucrose production. In 2011, about 168 million tonnes of sucrose was produced worldwide with a cane to beet ratio of approximately 5:1 [34].

General process description

The general process description is depicted in Figure 2.3. The first step in ethanol production from beet or cane sugar is hot water extraction of chipped and shredded plant material in a counter current extraction process. After the juice has been clarified, the pH and sugar content of the resulting sugary liquid are adjusted to optimal levels (juice concentration through evaporation). This is followed by pasteurization, cooling and inoculation of the juice with yeast, which initiates the biochemical conversion of sucrose to ethanol and carbon dioxide. Final

ethanol titers between 80-100 g/L are reached after two to three days during which the fermentation is cooled and agitated to keep process parameter optimal. The resulting beer is fed into a stripping and rectification process that yields 95% (v/v) ethanol, a mix of fusel alcohols and ethanol and vinasse (the ethanol deprived watery phase after rectification). Further dehydration of the ethanol to 99.5% (v/v) is achieved by binding the remaining water to a hydrophilic molecular sieve. The resulting bioethanol is then shipped off to be blended with gasoline.

Typically, the energy rich fibrous plant material that is leftover from the sugar extraction process (bagasse) is used to generate process steam and electricity. This makes the plant energetically self-sufficient and oftentimes with a net surplus of electricity, which can be sold to the local utility. Sugar cane or beet vinasse is rich in nutrients and can be used to irrigate the crops or sold as animal fodder. Alternatively, vinasse can undergo anaerobic digestion taking advantage of its high chemical oxygen demand [35]. The resulting methane can be burned to further increase the energy output of the plant or be fed into an existing pipeline system after purification. The effluent of the digester remains rich in nutrients and can facilitate crop growth when applied through irrigation.

The fermentation product carbon dioxide accrues in equimolar amounts as ethanol but has no caloric heating value. Because of its high inherent purity it is often compressed with minimal prior gas cleaning and sold to beverage companies. In an effort to sequester this by-product and generate additional biofuels, the generated CO₂ could be used as a feedstock for algae cultivation. In contrast to flue gas from power plants, which contain approximately 15% CO₂, the purity of fermentation-derived carbon dioxide is close to 100%. This would allow for a higher equilibrium concentration of the gas in the liquid phase and could increase algae growth. Additionally, toxic compounds that are commonly found in flue gases from power plants are completely absent in biochemically derived CO₂ making gas detoxification unnecessary.

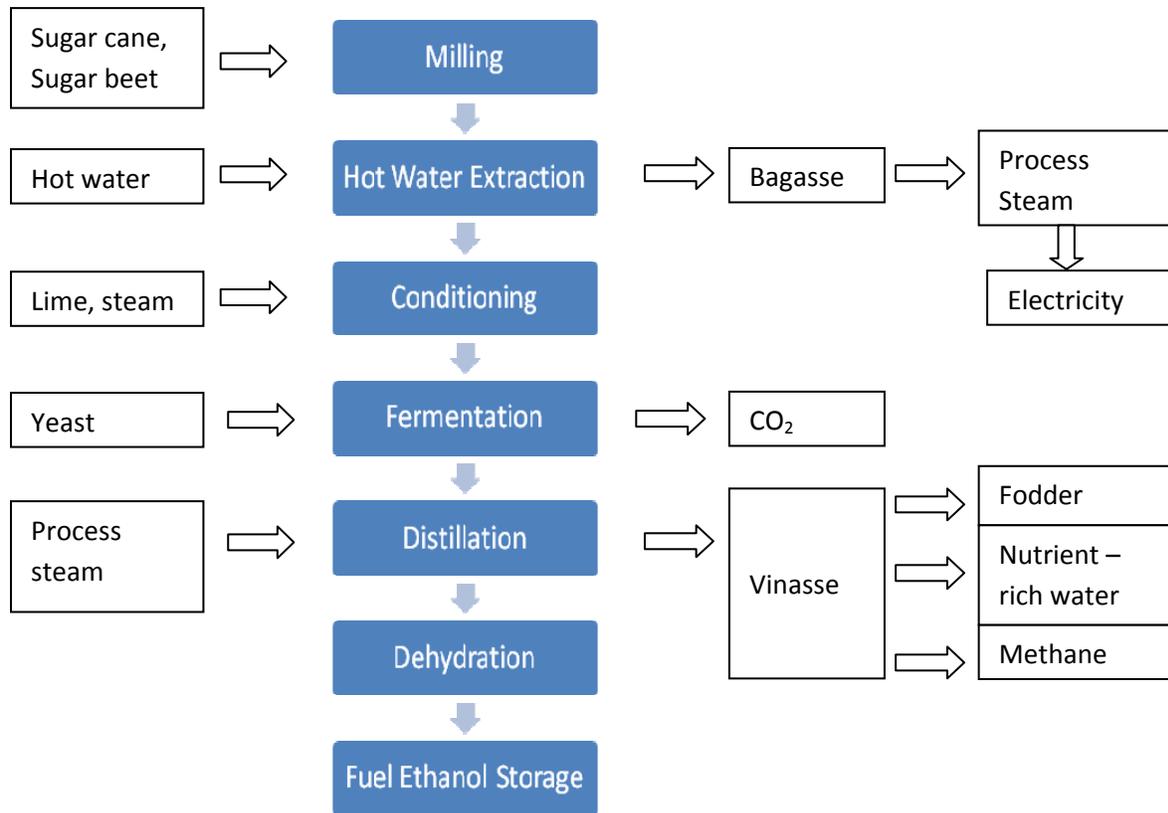


Figure 2.3. Flow chart of a sucrose-based fuel ethanol plant

Biofuel yield and energetic considerations

The Hawaii Bioenergy Master Plan [15] recognized cane sugar as the best sucrose producing crop in tropical climates. Consequently, all following calculations and assessments for the sucrose platform are based on sugar cane. Using historic production data, each tonne of burned and chopped sugar cane contains about 135 kg of fermentable sucrose. Assuming an ethanol yield coefficient of 141 gallons per tonne of fermentable sugar [10], each tonne of burned and chopped sugar cane yields about 72 L of pure ethanol. At the same time, 130 kg (dry weight) of bagasse are produced. Bagasse, the fibrous residue after juice extraction, is commonly burned to generate process heat and electricity. The average cane-to-ethanol facility in Brazil is capable of covering 100% of their on-site energy demands (both thermal and electric) and produce surplus electricity of about 6 kWh per tonne of processed sugar cane [36]. However, most of the existing

Brazilian plants employ a production process (in particular the rectification process) that is technologically outdated. Dias et al. [37] demonstrated that the specific energy demand can be reduced significantly if thermal integration (using Pinch technology) is applied. Their analysis showed that, depending on the process configuration, a maximum of 144 kWh surplus electricity per tonne of cane could be generated using a Biomass Integrated Gasification Combined Cycle (BIGCC). Less advanced but more standard thermal conversion units such as the Rankine Cycle with condensing steam turbine (RCCOND) would reduce surplus electricity output to 60-80 kWh per tonne of cane depending on the exact configuration. Still, this represents an increase of more than an order of magnitude when compared to the average electrical output of existing cane ethanol facilities in Brazil. Further calculations and comparisons in this report will be based on the thermally optimized scenario employing the RCCOND technology with a yield of 70 kWh of excess electricity per tonne of cane.

Vinasse, the liquid fermentation by-product following ethanol recovery, can contribute to additional biofuel production. Data from Wilkie et al. [30] suggest that for each gallon of cane-based ethanol produced, 16.3 gallons of vinasse are generated as well. Table 2.5 lists the average properties of this by-product (adapted from [38]).

Table 2.5. Properties of sugar cane vinasse [38]

pH	[-]	4.04±0.49
TCOD	[g/L]	30.4±8.2
Total solids	[g/L]	-
Total nitrogen	[mg/L]	628±316
Total phosphorus	[mg/L]	130±110
Potassium	[mg/L]	1,952±1,151

Due to its low solid content, production of animal fodder from vinasse is generally not practiced. Instead, vinasse is increasingly treated as a nutrient and water source for the sugar cane crop. However, the high organic load of vinasse entails significant methane and carbon dioxide emissions due to uncontrolled microbial digestion of the organic matter on the farmland.

Therefore, anaerobic digestion as a pretreatment before soil application has been suggested [21]. Based on a methane yield of 0.25 m³ per kg COD fed, a total of 8.8 m³ of methane per tonne of sugar cane can be generated. This represents about 20 percent of the chemical energy contained in the produced ethanol. Since all thermal power demands of a cane ethanol plant are met by burning bagasse, the biogas could be used to generate additional electricity. Based on the anaerobic digester/CHP platform, about 26 kWh of electricity per tonne of processed sugar cane could be generated, boosting the total electric output from 70 to 96 kWh per tonne of processed sugar cane for a modern cane ethanol facility employing state of the art thermal integration and power generation. Figure 2.4 and Figure 2.5 summarize the flow of energy and matter in the proposed sugar cane platform.

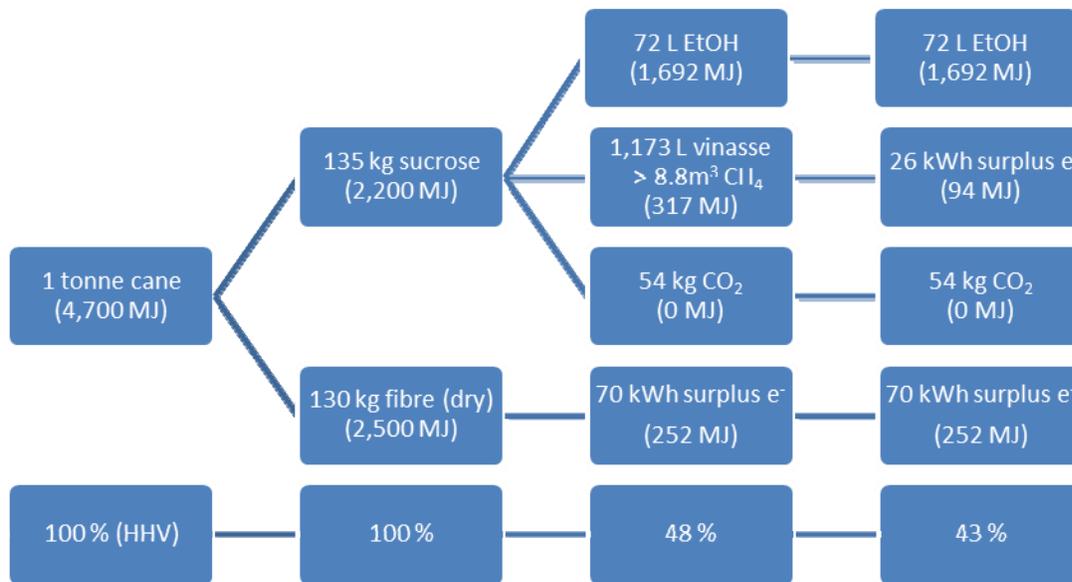


Figure 2.4. Conversion of one tonne of cropped and burned sugar cane with respect to mass and energy based in the Higher Heating Value (HHV) of each compound

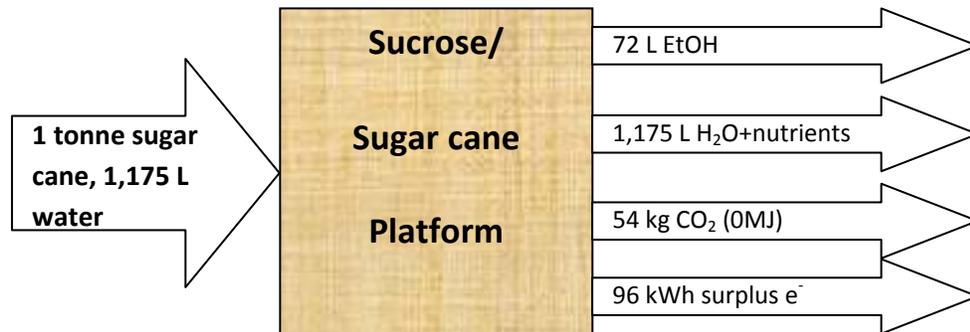


Figure 2.5. The sugar cane platform

Capital cost

Although investment cost for cane ethanol plants are dependent upon the specific location, expenditure data from existing facilities can be helpful to predict a reasonable range for the expected capital cost. Bake et al. [39] evaluated data on investment cost for autonomous cane ethanol plants in Brazil. It was found that plants built between the years of 1990-2000 had an average investment cost range of 30-35 million US\$ at an average plant capacity of at 240-500 m³/day ethanol (with an average of 190 processing days per year). Furthermore, a scale factor of S=0.67 could be identified. Using this data and applying the scaling equation

$$\frac{C_1}{C_2} = \left(\frac{Q_1}{Q_2}\right)^S \quad (2.2)$$

where C is the capital investment and Q is the plant output, the investment cost of new autonomous cane ethanol plant (without anaerobic digestion for additional heat and power generation) can be estimated using Figure 2.6.

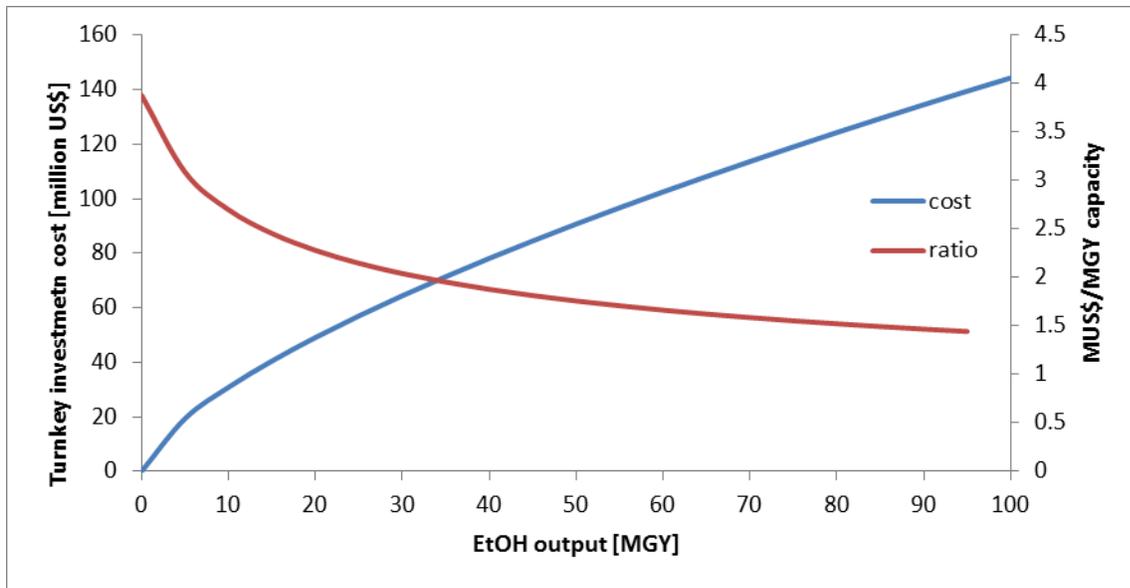


Figure 2.6. Turnkey investment cost of an autonomous cane ethanol plant using a scaling equation and data published by [39]

2.1.3 Starch Platform

Starch is a polymerized sugar that plants use to store energy for future use. Crops that are harvested for their high starch content include corn, potatoes, cassava, cereals etc. Cassava and corn are best adapted to tropical regions and can produce yields of around 12.5 and 19 tonnes of starch per hectare per year, respectively [21]. Currently, the vast majority of bioethanol produced in the United States is based on corn starch and amounts to 13.9 billion gallons [40]. More than 95% of the ethanol is blended with gasoline at the E10 level (10% ethanol) so that approximately 10% of the nation's motor fuel demand is covered by a renewable resource. Additionally, 39.4 million tonnes of livestock feed is produced as a co-product, replacing more than 45 million tonnes of traditional corn and soybean livestock feed rations annually.

Corn

General process description

Many microorganisms, including baker's yeast, are not capable of metabolizing starch directly. Therefore, prior to fermentation, starch needs to undergo hydrolysis to convert the polymerized

sugar into mono and disaccharides. In a corn-based dry milling process, this is typically done in two steps using enzymes. First, the enzyme alpha-amylase is added to liquefy the slurry (debranching of starch molecules). This is followed by the second enzymatic conversion of the debranched starch molecules to mono and disaccharides (saccharification). Often, fermentation is started while saccharification is still ongoing to increase speed and yield of the reaction. Figure 2.7 outlines the process in more detail.

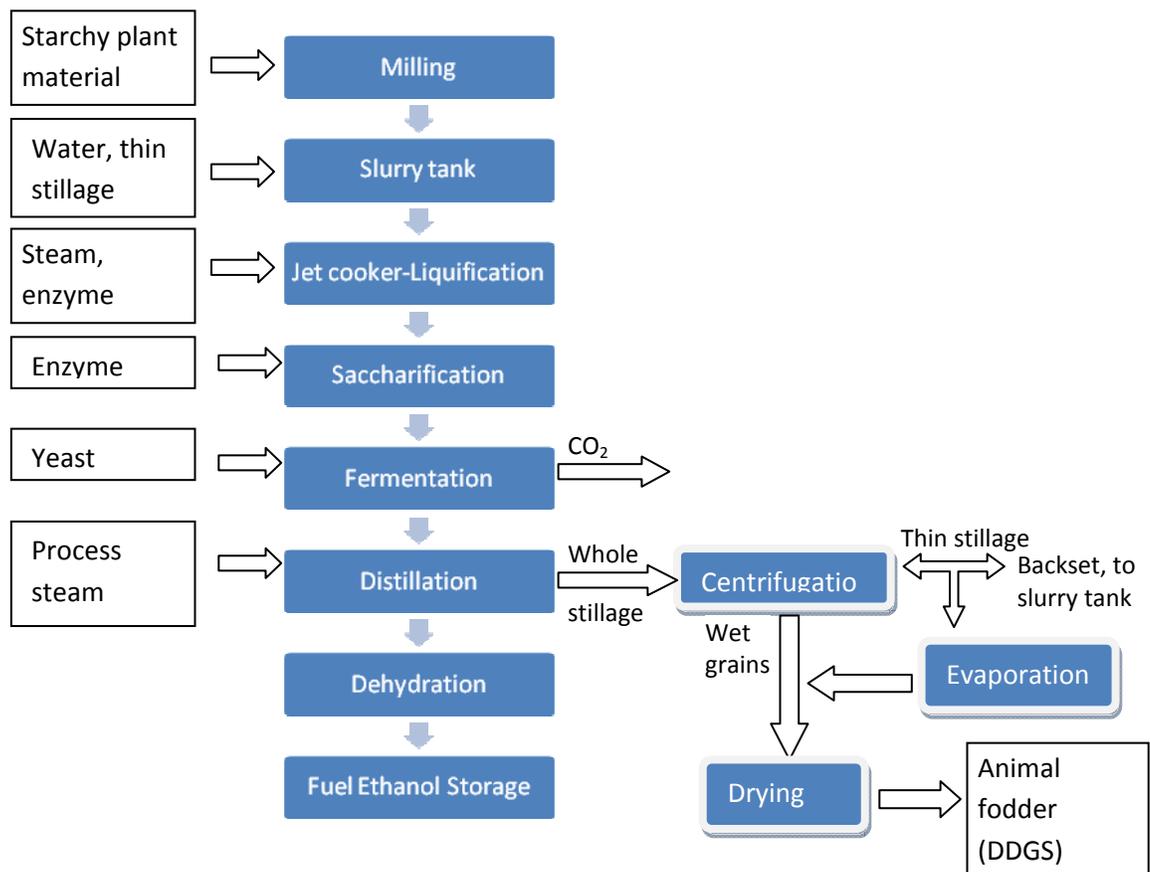


Figure 2.7. Flow chart of a starch-based fuel ethanol plant (dry milling)

Following distillation, the ethanol-deprived whole stillage is centrifuged to separate the solids from the liquid. The solids are sold as distiller’s wet grains, or are mixed with concentrated thin stillage followed by a drying process that yields distiller’s dry grains with solubles (DDGS).

DDGS have become a valuable co-product that contributes significantly to the profitability of a dry-mill ethanol plant.

The wet-milling process is different in that it allows for a broader spectrum of products to be produced from corn kernels (i.e. EtOH, corn oil, gluten meal, starches, high fructose corn syrup etc.). Since the capital requirements are significantly higher than for the dry milling process, commercial wet milling plants are typically three to five times larger to take advantage of the economy of scale. Due to limited amounts of farmland and therefore insufficient amounts of feedstock on small island states, the wet milling process will not be considered in this report.

Thin stillage

Unless a sufficiently large animal feedstock market could be developed in Hawaii, a potential dry mill corn ethanol plant would have to export the majority of the produced DDGS to a global market. South East Asia is already among the top ten DDGS importers according to the North American Institute for Beef Economic Research and Hawaii's geographical location would put it in closer proximity to this market than plants located on the main land. Alternatively, in order to reduce the amount of DDGS and increase its quality, Agler et al. [32] proposes to integrate thermophilic digestion of thin stillage into the process. Anaerobic digestion of thin stillage, that would otherwise be condensed and mixed with Distillers Wet Grains (DWG) to produce DDGS, yields bio-methane and eliminates the energy intensive step of thin stillage evaporation. Additionally, the amount of dried animal feedstock is reduced by about half [32], which cuts the energy demand for drying proportionately.

Energy demand of corn processing

Based on a new typical dry mill corn ethanol plant, about 935 kWh thermal and 66 kWh electrical energy per tonne of processed corn is used to produce 415 L ethanol and 280 kg DDGS [41]. When stillage evaporation is replaced by anaerobic digestion of thin stillage so that DDG is produced rather than DDGS, the thermal power demand reduces to 740 kWh per tonne of processed corn (estimate based on data from [32]). At the same time, the generated methane (118 m³/t processed corn, see Table 2.6) can be used to generate about 590 kWh process heat and 350

kWh electricity in a co-generation power plant (see anaerobic digestion/CHP platform). This reduces the thermal demand of the plant to 150 kWh/t (540 MJ/t) and produces a net gain of electricity of 284 kWh/t of processed corn. In an effort to eliminate the external thermal demand of the refinery, the thermal output of the CHP unit could be increased at the expense of electricity generation. Based on a 30% thermal efficiency of electricity generation, the surplus electricity would decrease to 238 kWh while the external thermal demand would be eliminated.

Table 2.6. Properties of thin stillage from a typical dry-grind corn-ethanol plant (data from [21])

pH	[-]	4.46
TCOD	[g/l]	94
Whole stillage yield	[m ³ /t corn]	5.0

Consequently, shifting away from DDGS to DDG combined with biogas production could not only offset all thermal power demands of the plant but also allow for a substantial co-generation of electricity that could be sold to the grid. Figure 2.8 illustrates the flow of matter and energy for both scenarios whereas Figure 2.9 reduces the process scheme to a platform based block schematic.

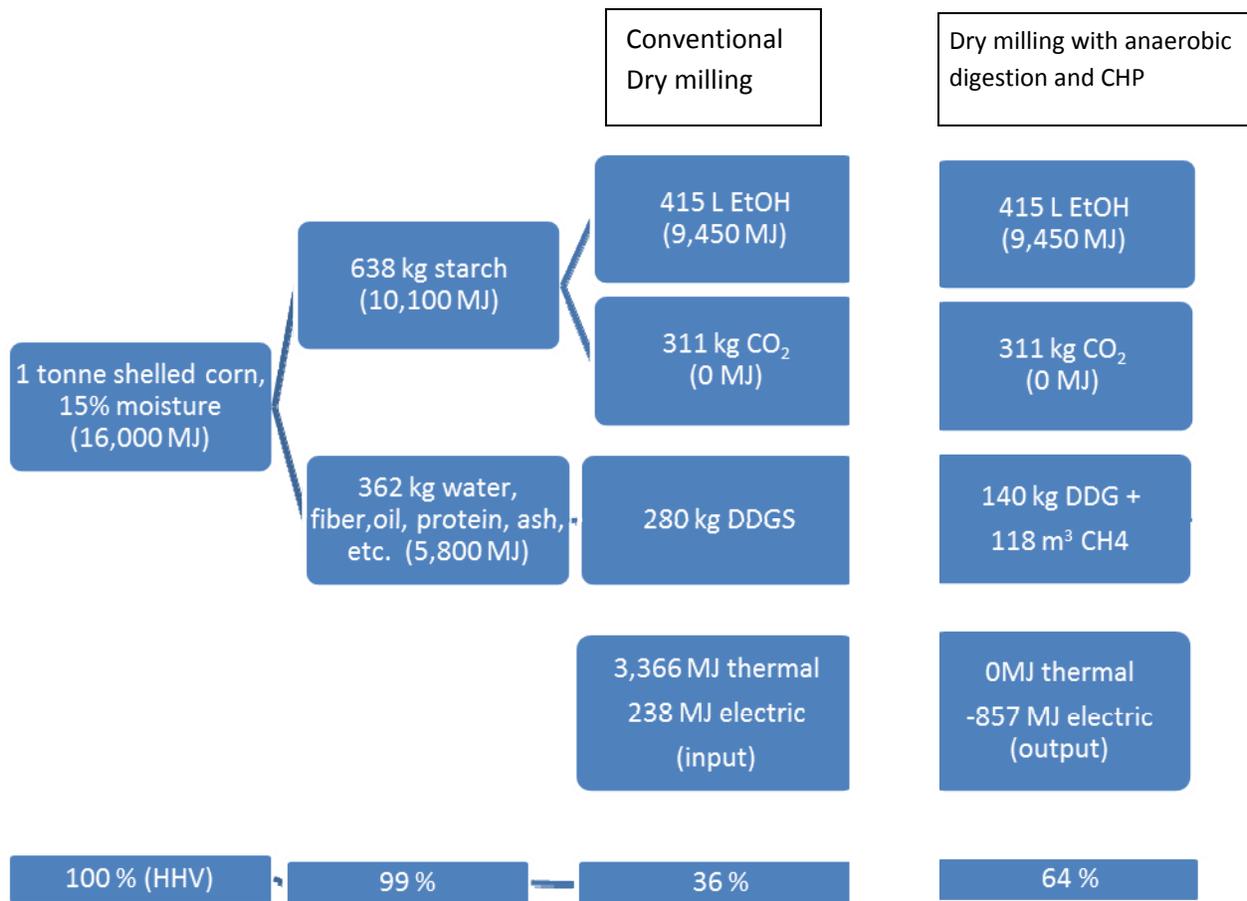


Figure 2.8. Flow of energy and matter in a typical dry mill corn-ethanol plant with and without anaerobic digestion of thin stillage

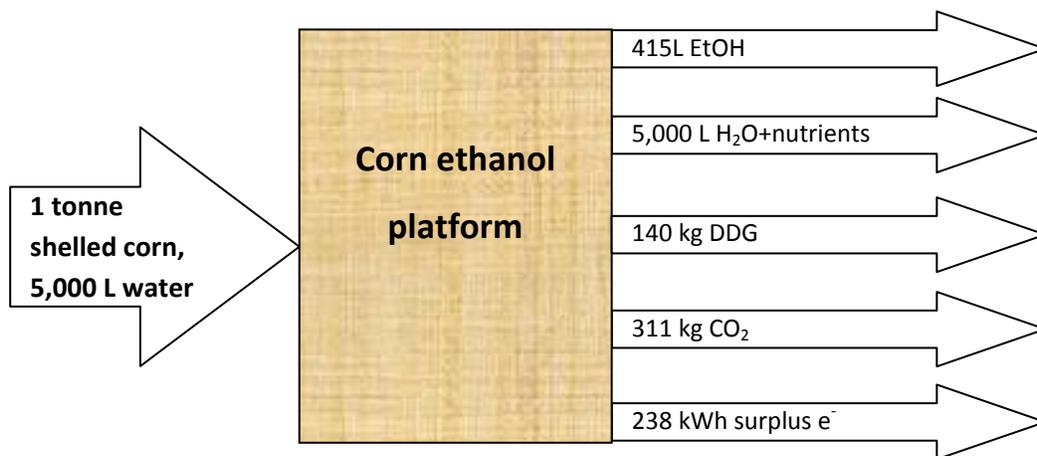


Figure 2.9. The corn ethanol platform (with built-in anaerobic digestion and CHP)

Capital cost for dry grind corn ethanol plants

The investment cost for corn based dry grind ethanol plants have been tracked and analyzed since the 70's and 80's. Kwiatkowski et al. [42] modeled the cost of fuel ethanol production for a dry grind ethanol plant and calculated the total capital investment cost with \$46.7 million for a 40 MGY plant. Hettinga et al. [27] identified a scaling factor of $s=0.67$ for recently established corn ethanol plants (dry grind). Using this data and applying the scaling equation (see above), the investment cost of turnkey autonomous dry grind ethanol plants can be estimated using Figure 2.10. It is important to point out that additional features, such as anaerobic digestion of thin stillage for heat and power generation, are not included in the estimate.

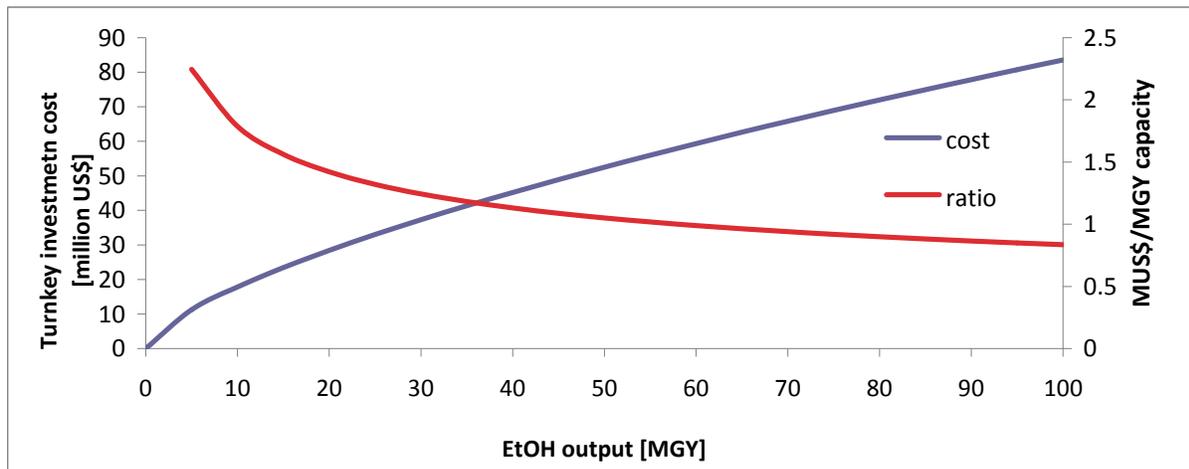


Figure 2.10. Turnkey investment cost of an autonomous dry grind ethanol plant using a scaling equation and data published by Hettinga, et al. [43]

Cassava

Cassava is a starchy tuber crop that traditionally serves as nourishment for countries in drought plagued regions of Africa [44]. In recent years, the plant has drawn increased interest as an energy crop due to its high starch content and yield, ease of cultivation, and high drought tolerance [45].

General process description

Unlike corn, cassava stores its starch in the root system below the surface. Conventionally, the tubers are harvest manually due to the availability of cheap labor in lesser developed countries. Alternatively, a modified mechanical harvesting system, similar to a potato harvester, is imaginable [21]. The tubers are often chipped and sun dried prior to processing to reduce transportation cost and increase shelf life. However, direct milling followed by mashing seems feasible if the tubers are processed within a reasonable distance of the conversion facility. The unit operations following mashing are similar to a dry mill corn ethanol plant and deviate only with respect to stillage treatment.

Thin stillage

Due to the high viscosity and low nutritional value of cassava stillage, production of animal fodder is considered unattractive [46]. Therefore, anaerobic digestion is suggested to decrease high TCOD loadings of 40-70 g/L [46] and generate combustible biogas. Based on the values given in Table 2.7, each tonne of processed cassava tubers yields approximately 29 m³ of methane in addition to ethanol. The chemical energy contained in the methane can be converted to 146 kWh of process heat and 88 kWh of electricity based on the co-generation power plant (see anaerobic digester/CHP platform).

Table 2.7. Assumptions for methane production from cassava whole stillage

Ethanol yield [L/tonne of tubers]	163
Stillage yield [L/L EtOH]	12
TCOD stillage [g/L]	60

Energy demand of cassava processing

If the specific energy consumption of the cassava plant is assumed to be half of that of a dry mill ethanol plant due to the absence of fodder production and therefore lack of drying needs [41], the net energy demand of the plant can be estimated as follows:

Specific energy demand of corn dry mill plant	Thermal: → 938 kWh/gal EtOH Electric: → 0.75 kWh/gal EtOH
Specific energy demand of a cassava plant without anaerobic digestion	Thermal: → 469 kWh/gal EtOH or 202 kWh/t of tubers Electric: → 0.375 kWh/gal EtOH or 16 kWh/t of tubers
Energetic yield from anaerobic digestion	Thermal: → 146 kWh/tonne of tubers Electric: → 88 kWh/tonne of tubers
Net-specific energy demand of a cassava plant with anaerobic digestion and co-generation of steam and electricity (CHP)	Thermal: → 56 kWh/tonne of tubers Electric: → -72 kWh/tonne of tubers
Net-specific energy demand of a cassava plant with anaerobic digestion and co-generation of steam and electricity (CHP) and eliminated external thermal demand	Thermal: → 0 kWh/tonne of tubers Electric: → -55 kWh/tonne of tubers

Again, the co-generation of electricity and steam leads to a drastic reduction of thermal demands and yields a surplus of electricity that can be sold to the grid. In an effort to eliminate the external thermal demand of the refinery, the thermal output of the CHP unit could be increased at the expense of electricity generation. Based on a 30% thermal efficiency of electricity generation, the surplus electricity would decrease to 55 kWh while the external thermal demand would be eliminated. The flow of matter and energy are depicted in Figure 2.11 and Figure 2.12.

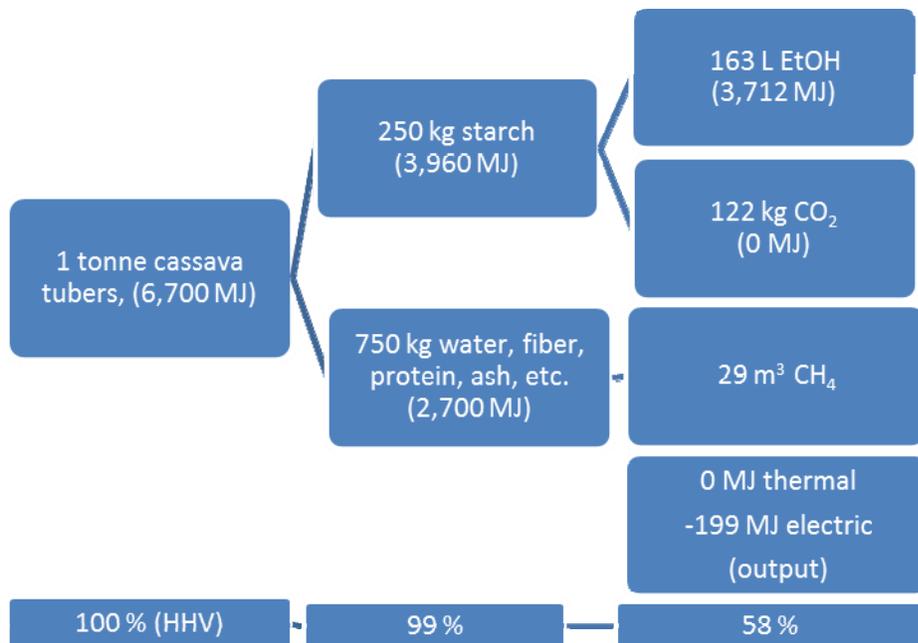


Figure 2.11. Flow of energy and mass of a cassava to ethanol plant

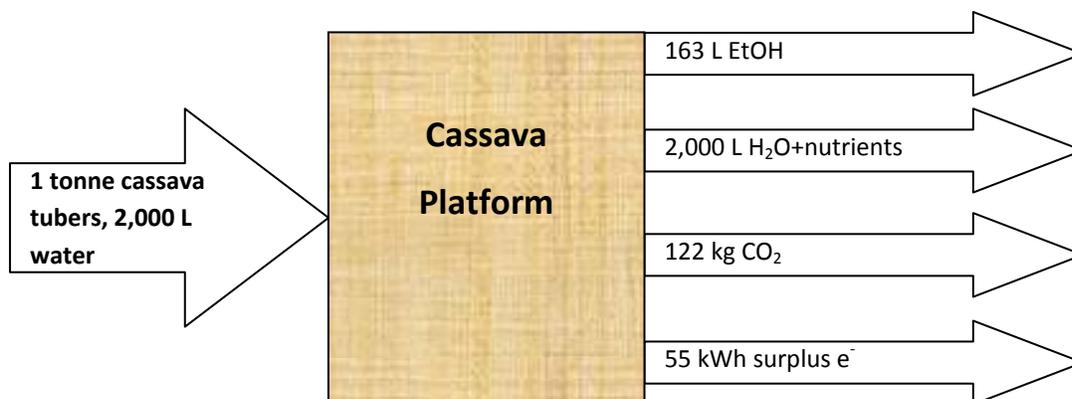


Figure 2.12. The cassava platform

Capital cost for cassava ethanol plants

In contrast to corn, cassava has only recently gained attention as a feedstock for ethanol production. Of the few existing plants, most are located in Thailand and China, where cassava

has been used traditionally as food source for livestock and humans. Consequently, investment cost estimates are scarce and should be viewed with caution. In fact, Sorapipatana's work [47] on the life cycle cost of ethanol from cassava in Thailand provides the only data used in this report for turnkey investment cost, as shown in Figure 2.13. Based on industrial quotes and estimates, the total capital cost were estimated to be \$30 million for a 14.5 MGY plant.

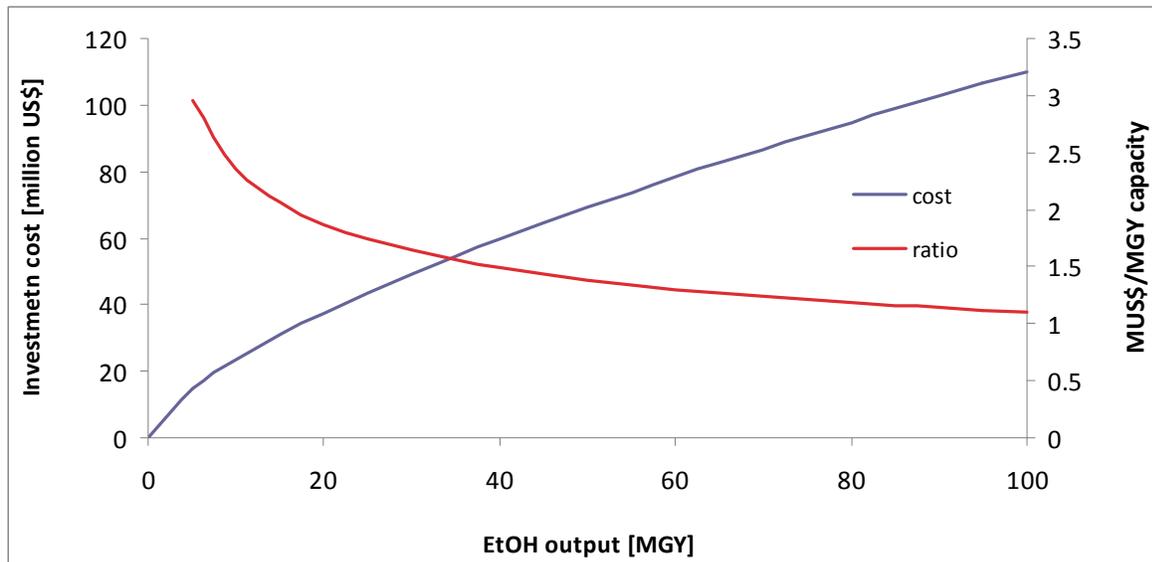


Figure 2.13. Turnkey investment cost of an autonomous cassava ethanol plant using a scaling equation with a scaling factor of 0.67 and data published in [47]

2.1.4 Lignocellulosic Platform

Lignocellulosic biomass, such as woody biomass, agricultural residues (e.g. corn stover, bagasse) and dedicated energy crops (e.g. banagrass, switchgrass, etc.), is rich in cellulose, hemicellulose and lignin. Since the human digestive system is incapable of digesting cellulosic biomass, the food versus fuel argument becomes less problematic. However, energy crops competing with food crops for farmland remains a concern.

Despite substantial progress in lignocellulosic ethanol research, production costs for ethanol are still substantially higher than for a typical dry mill corn-to-ethanol plant (see Table 2.8). Moreover, commercial cellulosic ethanol plants are only now starting to come online, with Beta Renewables 13 MGY cellulosic plant in Italy being the first [48]. However, at construction cost of about \$12/gal ethanol capacity or six to eight times that of a dry mill corn ethanol plant [48], commercial success remains to be proven. Substantial support for lignocellulosic ethanol was enacted in the Energy Independence and Security Act of 2007 that requires the production of 21 billion gallons of ethanol from cellulosic feedstocks by 2022 [49]. Moreover, the 2008 Farm Bill provided \$1.01 per gallon subsidy for cellulosic ethanol [49]. It is anticipated that both will lead to a significant increase in cellulosic ethanol.

Pretreatment and Hydrolysis

As stated before, lignocellulosic biomass consists of cellulose (appr. 50%), hemicellulose (appr. 20%) and lignin (appr. 30%). On a molecular level, the polymers of six and five carbon sugars (cellulose and hemicellulose) are arranged in such a way, that they bind strongly to lignin in order to provide structural stability, decrease water solubility and resist microbial digestion. Primarily, lignocellulosic biomass is found in terrestrial plant cell walls where the functions listed above are critical. Therefore, in order to effectively convert cellulose and hemicellulose biologically to biofuels, the feedstock has to undergo extensive pretreatment that can involve a combination of physical, thermal, chemical and biological steps to overcome the “recalcitrance” to biochemical conversion. Lignin, as it cannot be used biochemically to produce ethanol, is removed as part of the pretreatment process and is typically burned to generate heat and electricity for on-site consumption. A list of popular pretreatment techniques and the projected cost of lignocellulosic ethanol is given in Table 2.8.

Table 2.8. Expected production cost of ethanol from lignocellulosic biomass based on the pretreatment process at two scales [30]

Pretreatment	Biomass cost: \$50/tonne (dry matter)	
	Ethanol (\$/gal) 25 MGY	Ethanol (\$/gal) 5 MGY
Corn ethanol (50 MGY dry mill, mainland 2008)	1.05	
Concentrated acid hydrolysis, neutralization and fermentation	2.28	2.76
Ammonia disruption hydrolysis and fermentation	1.81	2.4
Steam disruption, hydrolysis and fermentation	1.63	2.15
Acid disruption and transgenic microorganism fermentation	1.86	2.45
Concentrated acid hydrolysis, acid recycle and fermentation	1.86	2.19
Acidified acetone extraction, hydrolysis and fermentation	1.7	2.13

Similar to starch, cellulose is also a polymer of glucose. Unlike the starch molecule, where individual glucose molecules are arranged in a α -1,4 linkage, the glucose molecules in cellulose are linked through a β -1,4 bond (see Figure 2.14). This seemingly insignificant difference in arrangement leads to a much higher resistance to microbial degradation. Consequently, most microorganisms, including yeast, are not capable of digesting cellulose. Therefore, following pretreatment, the polymerized sugars need to undergo hydrolysis. Although there is an abundance of hydrolysis techniques, they generally fall into one of two categories: chemical and biochemical hydrolysis. Chemical processes typically use dilute or concentrated acids or bases whereas biochemical approaches rely on enzymes. Both methods have strengths and weaknesses and as of today, both concepts are being followed in parallel in research and commercially.

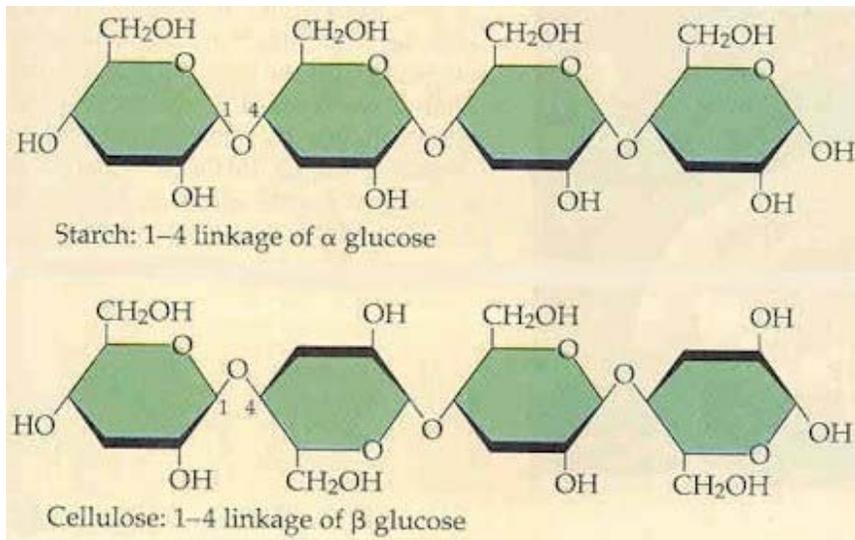


Figure 2.14. Difference of starch and cellulose on a molecular level [50]

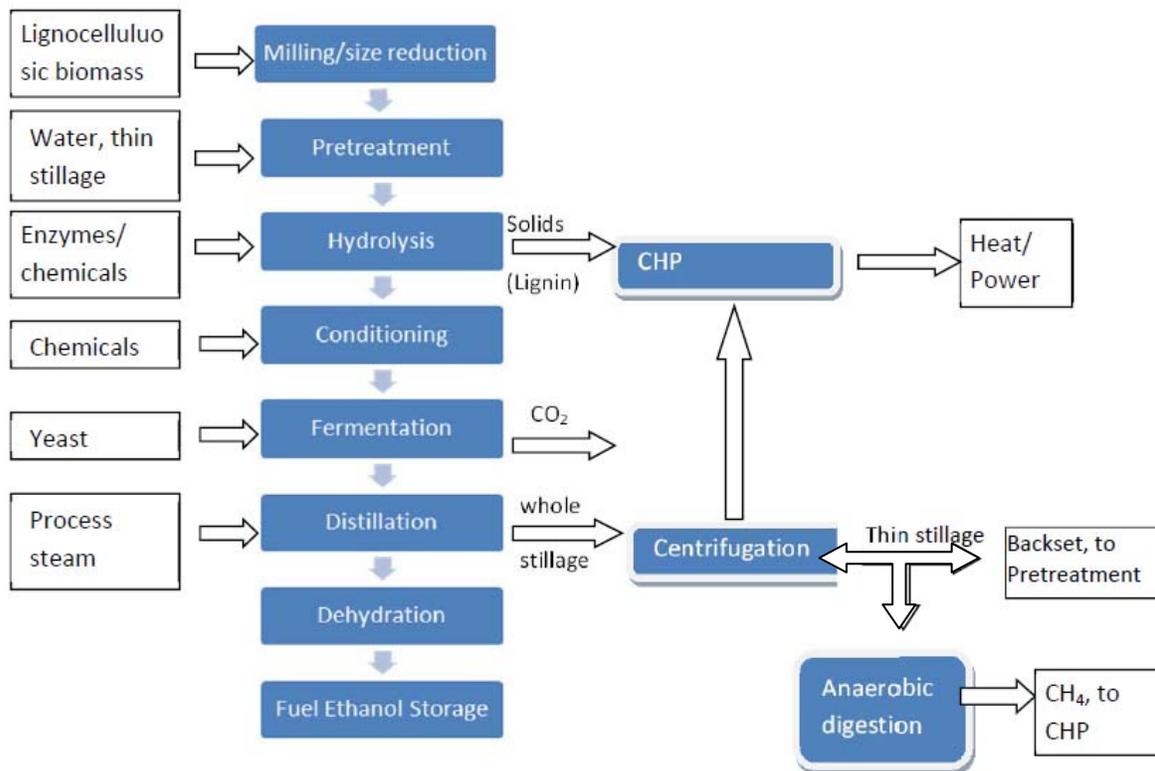


Figure 2.15. Flowchart of a lignocellulosic ethanol plant based on hydrolysis

The unit operations following pretreatment and hydrolysis are similar or identical to any of the ethanol platforms described above (see Figure 2.15). Dissimilarities exist, depending on the toxicity of the pretreatment/hydrolysis reaction, with respect to detoxification (broth conditioning) and sterilization. Due to the severity of the pretreatment process (high temperatures, low pH, and high pressure), sterilization of the fermentation broth can usually be omitted.

Energy balance for lignocellulosic feedstocks

The National Renewable Energy Laboratory [51] issued a detailed report on the production of ethanol from lignocellulosic plant material (corn stover) using the process of dilute acid pretreatment and successive enzymatic saccharification and fermentation [52]. The report is extensive and provides a detailed analysis of mass, energy and economic balances for the conversion process. Their analysis is based on quotes and data provided by the industry for conversion efficiencies and equipment cost. Due to the depth and detail provided, this report will draw heavily on facts and conclusions in the NREL report. Key data that led to the simplified balances depicted in Figure 2.16 and Figure 2.17 is provided in Table 2.9.

Table 2.9. Basic assumptions for mass and energy balance of cellulosic ethanol plant [52]

Sugar yield	535 kg/t biomass [53]
Ethanol yield	298 L/t biomass [53]
Fermentation efficiency	90 %
Boiler efficiency	80 %
TCOD waste water	65 g/L
Specific waste water production	15.1 L/L EtOH

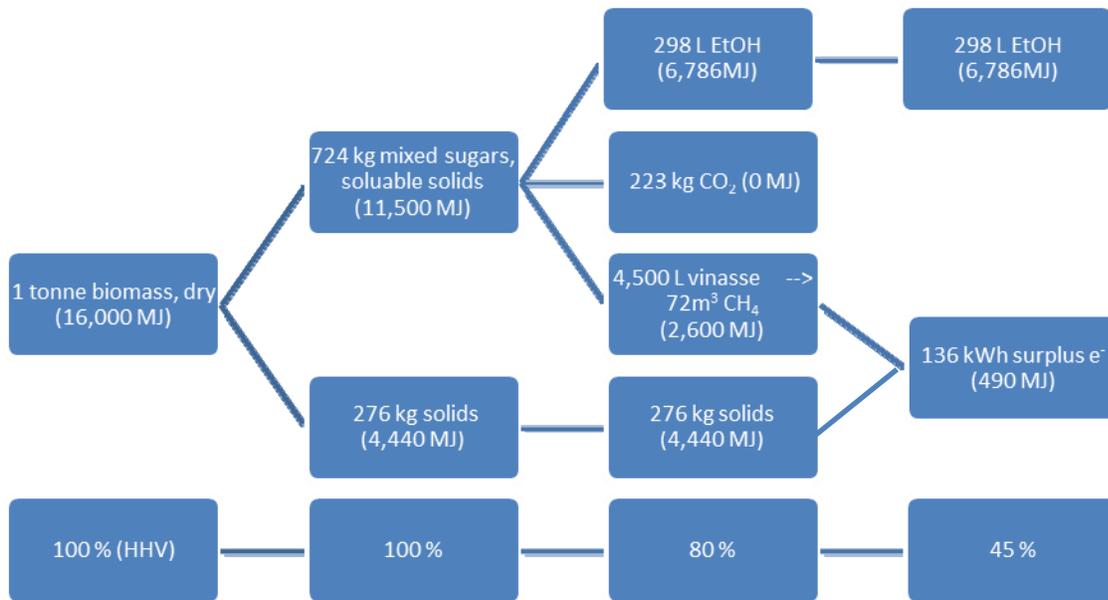


Figure 2.16. Flow of matter and energy in a cellulosic ethanol plant based on [52]

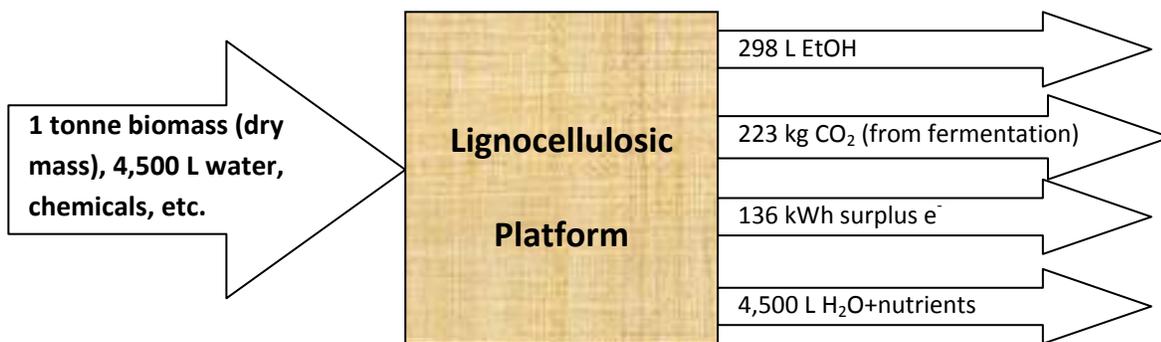


Figure 2.17. Lignocellulosic platform

Capital cost for a cellulosic ethanol plant

As stated earlier, commercial cellulosic ethanol plants are only now starting to come online, with Beta Renewables' 13 MGY (million gallons per year) cellulosic plant in Italy being the first one [48]. Consequently, reliable cost estimates based on existing plants are not available at this point. Additionally, costs are expected to vary significantly based on the technology used. Therefore, existing appraisals for turnkey cellulosic ethanol plants are always based on a specific technology and rely heavily on quotes and estimates. For example, the NREL report [52] based its cost data on industrial quotes and estimates and found the total investment cost for a 61 MGY plant (dilute acid pretreatment and enzymatic hydrolysis) to be \$422 million.

2.1.5 Yield Analysis of Sugar, Starch and Lignocellulosic Platform

Based on the previously established conversion platforms for sucrose (sugarcane), starch (corn and cassava) and lignocellulosic biomass (banagrass), a side by side comparison of the potential yields with respect to biomass, fermentable sugars, ethanol, bio-methane, electricity generation and animal feed generation on a per acre bases is possible (see Table 2.10). Additionally, thermal inputs and qualitative fertilizer/water requirements are provided.

Results from this analysis show that the highest ethanol yield per acre can be achieved through lignocellulosic conversion of banagrass (6,407 L), followed by sugar cane (3,600 L), corn (3,325 L) and cassava (3,300 L). The maximum electricity per acre of farmland, in addition to the main product ethanol, can be generated through sugar cane processing with 4,800 kWh, whereas the lignocellulosic ethanol conversions yields approximately 2,900 kWh. Cassava-to-ethanol and corn-to-ethanol have the lowest electricity yield with 1,904 and 1,100 kWh, respectively. However, thermal conversion of the woody plant parts above ground could increase these values.

Of the crops investigated, the corn platform is the only technology that generates high quality animal fodder (DDG) as byproduct. Since DDG is a commodity traded globally, it could be sold throughout the world. Alternatively, it could also be used to supplement local feed rations for animals used in meat, egg and milk production and decrease the states reliance of imported

livestock products. For perspective, 1.1 tonnes of DDG can replace about 1.3 tonnes of corn in a cattle feed-lot (RFA-reference [19]). On average, this is enough fodder to bring one head of cattle to its finishing weight [54]. It should be noted that additional ethanol/electricity output could be generated by converting agricultural waste from corn, sugar cane and cassava farming through the lignocellulosic platform as described and assessed in Section 2.1.4.

Table 2.10. Yield analysis of sugarcane, corn, cassava and banagrass based on their corresponding platform technologies

[per acre per year]	Cane	Corn	Cassava	Banagrass
Biomass [t]	50 ^a	8 ^c	20 ^e	21.5 ^f
EtOH [L]	3,600	3,325 ^d	3,300	6,407
CH ₄ from stillage [m ³]	456	945	580	1,550
Thermal input [kWh]	0	0	0	0
Electricity output to grid [kWh]	4,800	1,904	1,100	2,920
Animal Feed [t]	0	1.1 (DDG)	0	0
Fertilizer ⁱ [kg N/ha] / water requirements ⁱ [mm]	150 ^j / 1,500-2,000 ^j	157 ^k /600 ^l	100 ⁿ / 1,200-1,500 ^m	200 ^p / 1,500-2,000 ^o

^a burned and cropped, irrigated average historic yield on Hawaiian islands; ^b includes molasses sugar;

^c shelled corn, two harvests per year averaging each 160 bu/acre, based on field trials on Oahu; ^d 2.8 gal/bushel; ^e fresh tuber weight;

^f expected dry yield; ^g 79 gal/tonne dry matter; ^h includes electricity from bio-methane; ⁱ per harvested crop; ^j [22]; ^k [11, 12]; ^l [12]; ^m estimated from data by [13]; ⁿ [14]; ^o data not available but expected to be similar to sugar cane; ^p [55]

2.2 Chemical Conversion Platform

In this report, the term “chemical conversion platform” is limited to the transesterification reactions of fats (triglycerides) with alcohols (methanol, ethanol) to form biodiesel (fatty acid methyl and ethyl esters - FAME and FAEE, respectively) and glycerol. FAME and FAEE have a 38% higher energy density than ethanol and can be used as substitutes for petroleum based diesel.

With the exception of animal fats, most triglycerides are derived from either terrestrial plants (e.g. soy, canola, palm oil, etc.) or aquatic microorganism (e.g. algae, cyanobacteria, etc.). Often, used cooking oil/fats are collected as a feedstock for biodiesel production, but direct conversion of farmed vegetable oil to biodiesel offers the prospect for larger scale operations.

As the names imply, growing conditions for terrestrial and aquatic oil producers differ dramatically. Moreover, vegetable fats and oils can primarily be found in plant seeds whereas aquatic algae store triglycerides intracellularly. Consequently, harvest and pretreatment of plant and cell matter differ greatly. Therefore, this chapter will have separate sub-sections for harvest and pretreatment of terrestrial and aquatic plant and cell matter.

2.2.1 Harvest and Pretreatment of Terrestrial Oil Plants

Oil production from terrestrial oil plants was established many decades ago. Most widely cropped vegetable oils include rapeseed, sun flower and soy for the temperate climate zones and oil palm and coconut oil for the (sub) tropical regions. Harvesting techniques vary depending on plant physiology and can be highly mechanized (e.g. rapeseed, sun flower and soy) or rely on partly mechanized techniques and manual labor (palm oil). Harvested oil-containing plant parts are transported to a processing facility where mechanical pressing and/or solvent extraction is used to separate the oil from fibrous plant material. Residual biomass can be converted to animal feed (e.g. soy protein), burned for electricity generation, reapplied on farmland as mulch or anaerobically digested to yield biogas and nutrient rich water.

2.2.2 Harvest and Pretreatment of Aquatic Oil Producers

Most commonly used aquatic oil producing organisms are unicellular bacteria (e.g. cyanobacteria) or microalgae. They are usually autotrophic (self-feeding, i.e. utilizing sun light to produce plant matter from CO₂ and water), but heterotrophic microalgae (they grow in the dark by consuming sugars that are in solution) are being utilized for oil production as well [56]. Typically, oils are stored intracellularly, so that cell harvest and cell lysis (disruption of cell walls) is necessary. Many algae species considered for biofuel production can grow in brackish water with high salinity. Therefore, they do not necessarily have to compete with land or water intended for food or energy crop production.

Due to their microscopic size, cell harvest of microalgae is not trivial. Frequently used techniques include centrifugation, floatation, filtration or a combination thereof. The concentrated mixture of cells and water is then subjected to cell lysis which can be accomplished mechanically (e.g. ultrasound, blades), biologically (e.g. enzymes), thermally or chemically. The liberated oils do not mix with the watery broth which greatly simplifies product separation. The remaining broth is rich in nutrients and trace elements and is often recycled back to the bioreactor.

2.2.3 Transesterification and Process Description

Plant oils and lipids from aquatic microorganism (vegetable oils) are typically esters of a long chain fatty acid with glycerol as depicted in Figure 2.18. In order to reduce vegetable oil's higher viscosity and surface tension (when compared to diesel derived from crude oil), the glycerol in its structure is replaced with a short-chain alcohol such as methanol or ethanol to yield fatty acid methyl or ethyl esters (FAME or FAEE, respectively) and glycerol. The reaction is often carried out in semi-continuous batch reactors followed by product removal (phase separation). The by-product glycerol is commonly contaminated with unreacted short-chain alcohol and catalyst which needs to undergo purification prior to sale or disposal. During this process, the short-chain alcohol is recovered and recycled back into the process. Figure 2.19 Schematics of a biodiesel plant.

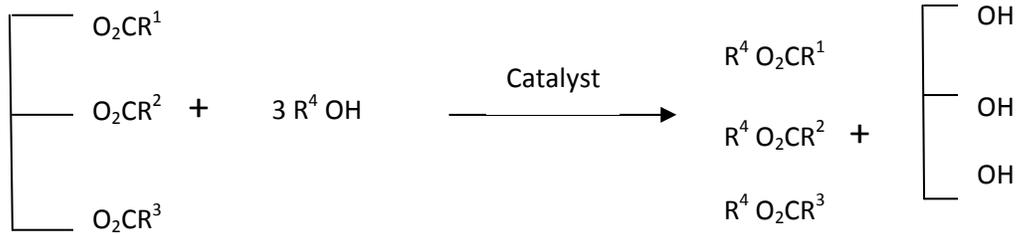


Figure 2.18. Transesterification reaction for biodiesel production from vegetable oil: R^1, R^2, R^3 - medium chained alkyl groups (C_{14} - C_{18}); R^4 - short chained alkyl group (C_1, C_2)

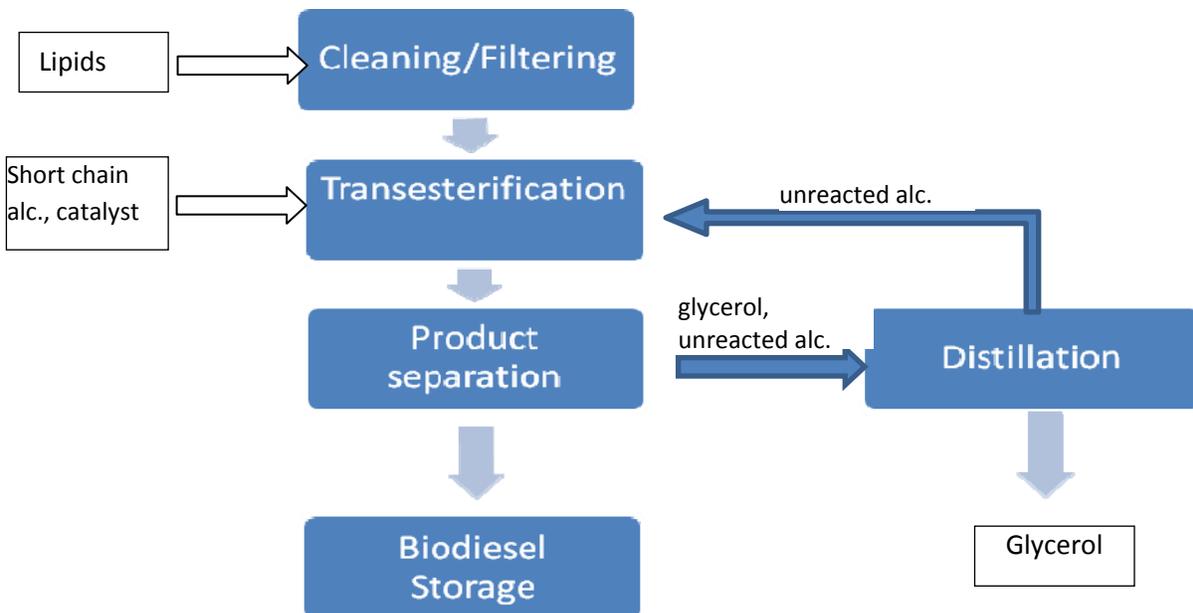


Figure 2.19. Schematics of a biodiesel plant

2.2.4 Energy Balance for Biodiesel Production

Depending on the origin of vegetable oils (aquatic or terrestrial) and the selected lipid extraction process, energetic inputs, in the form of heat and electricity, vary greatly. Xu et al. [9] calculated a combined thermal and electric demand of 0.22 MJ per MJ biodiesel for the production of

vegetable oil from microalgae using the dry route (mechanical and thermal drying of the algae prior to oil extraction). Soybean oil, representative for the majority of terrestrial oil plants, requires approximately 0.08 MJ per MJ biodiesel according to a study conducted by the National Renewable Energy Laboratory [51, 57]. Due to the wide spread of energetic inputs necessary to arrive at vegetable oil, the chemical conversion platform will be evaluated with vegetable oil as initial input.

The transesterification process is distinctive in its low technological requirements and modest energy demands. The largest energetic input is the added short chain alcohol with 0.08 MJ, followed by a thermal and electric power demand of 0.05 and 0.01 MJ per MJ of biodiesel, respectively [9].

The byproduct glycerol is traditionally purified and sold as a commodity or combusted. However, lately, the abundance of crude and purified glycerol has been exceeding the commercial demand so that alternative uses for glycerol have been proposed. Among these, anaerobic digestion for biogas production has been suggested by several authors [9, 58, 59]. Lopez et al. [58] reports a TCOD of 1,010 g/kg for crude glycerol from a biodiesel plant in Spain with a yield coefficient of approximately 0.3 m³/kg TCOD. Based on this data and assuming a more conservative yield coefficient of 0.25 m³/kg TCOD, 27 m³ of methane per kg of crude glycerol can be generated, which translates to 286 MJ of electricity and 477 MJ of thermal energy when the CHP platform technology is applied. The electric and thermal requirements per tonne of vegetable oil are 373 and 1,865 MJ, respectively, leaving a net consumption of 87 MJ (24 kWh) of electricity and 1,390 MJ of thermal energy. Figure 2.20 depicts the flow of mass and energy as described.

Capital Cost for a Biodiesel Plant

In a recent techno-economic analysis of a biodiesel biorefinery, Vlysidis [60] estimated the total capital cost for a 2.4 MGY plant to be €5.5 million or \$7.2 million (exchange rate of 1.3 Euro/US\$). Haas [61] performed a similar analysis and estimated the total investment cost to be \$11.4 million for a 10 MGY plant. Pacific Biodiesel recently (summer 2012) established a 5.5 MGY biodiesel plant on the Big Island, which required \$12 million investment capital [62]. The

wide spread of investment cost per annual plant capacity is indicative of a relatively low scaling factor. Figure 2.21 predicts total investment cost per annual plant capacity based on Haas's data and a scaling factor of 0.6.

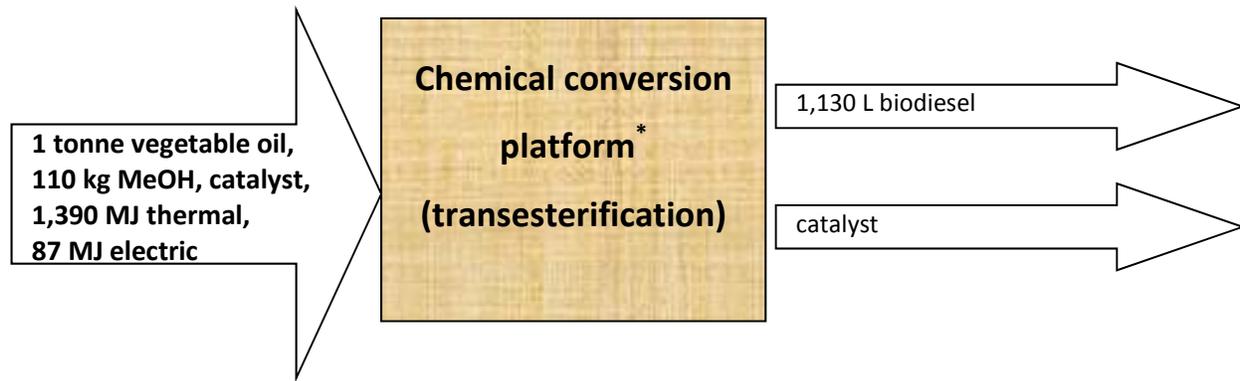


Figure 2.20. Block flow diagram of the chemical conversion platform

(*Anaerobic digestion of glycerol and CHP incorporated)

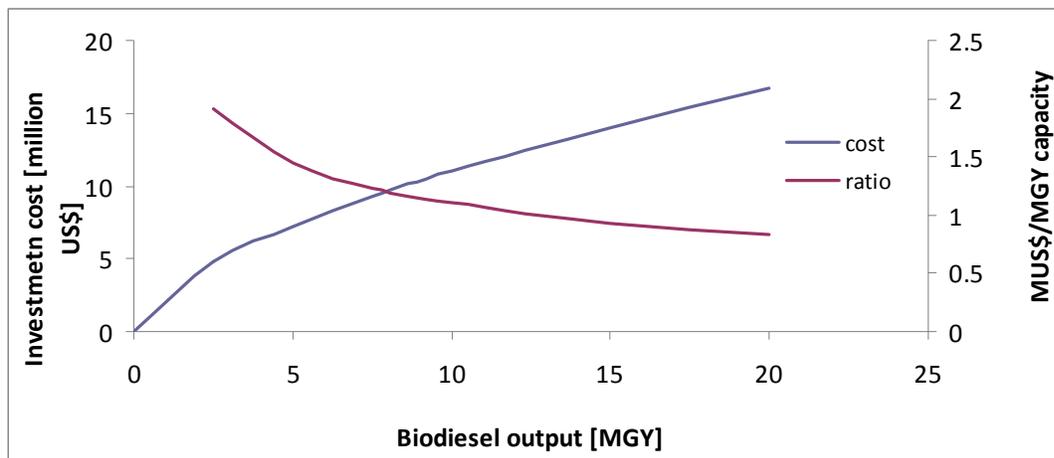


Figure 2.21. Turnkey investment cost of an biodiesel plant using a scaling equation with a scaling factor of 0.6 and data published by [61]

2.2.5 Yield Analysis of Terrestrial and Aquatic Oil Producers

Based on the chemical conversion platform, a side-by-side yield analysis for terrestrial and aquatic oil producers can be established and is depicted in Table 2.9. For this comparison, *Jatropha* is chosen as the terrestrial oil crop whereas micro algae represent aquatic lipid producers. Palm oil is excluded from this evaluation due to the lack of Hawaii-specific yield data. Vegetable oil yield per acre was established using data from [16] and NREL report [17].

Table 2.11 illustrates that micro-algae have the potential to outperform *Jatropha* plantations by a factor of sixteen. However, if the goal is to be competitive with fossil diesel, both approaches yield projected production cost that are not economical.

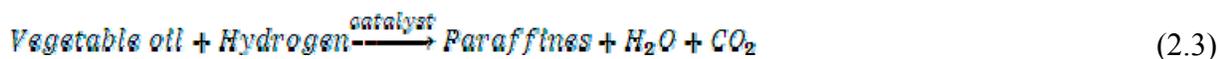
Table 2.11. Yield projections of terrestrial (*Jatropha*) and aquatic (micro-algae) oil producers

[per acre per year]	<i>Jatropha</i>	Micro-algae
Vegetable oil [L]	431 ^a	7,000 ^b
Biodiesel [L]	444	7,190
Thermal input ^c [MJ]	132	2,140
Electricity input from grid ^c [MJ]	8	136
Projected production cost for lipids [\$/gal]	18.70 ^a	5.30 ^d

^a Based on [16]; ^b based on trials averaging 20 g/m²/day with 20% lipids [17]; ^c Energetic utilization of oil cake not considered; ^d Based on [63]

2.2.6 Hydrogenation of Vegetable Oil

The hydrogenation of vegetable oil serves the purpose to catalytically reduce the oxygen content of triglycerides by reacting them over a catalyst in the presence of hydrogen according to the following reaction:



Paraffin refers to a mixture of hydrocarbons of which about 75 to 85% fall into the “green diesel” category, about 5 to 7% are gaseous and 1 to 7% are naphtha [21]. The resulting “green diesel” has energy content similar to fossil diesel, can be blended at any ratio with fossil diesel, reduces tailpipe emissions and has a long shelf life [64]. However, hydrogenation (sometimes referred to as “upgrading”) typically requires both high temperatures and pressure for an efficient reaction which translates to high capital cost for the process. Additionally, a cheap and, ideally, renewable hydrogen source is needed.

Commercialization is well under way with upgrading facilities located in Ireland (ConocoPhillips process), Finland and Singapore (NesteOil’s NExBTL process) [64].

2.3 Other Biochemical /Chemical Platform Technologies

Many of the platform technologies discussed in the preceding sections are in the process of being commercialized or have been deployed on a commercial scale already. Table 2.12 aligns commercial enterprises with the deployed technology, the desired product and the status of the operation with respect to scale (lab-, pilot-, demo-, and commercial scale). In addition to the previously discussed platform technologies, Table 2.12 also includes companies that utilize biochemical conversion technologies which are often proprietary in nature and that have not been realized on a commercial scale. Examples include algae farming (Sapphire Energy, Solazyme, Algenol, Aurora Biofuels, etc.), syngas fermentations (Coskata), butanol fermentations (Cobalt, Gevo, etc.), advanced lignocellulosic fermentations (ZeaChem, BlueFire Ethanol, LS9, Raven Biofuels, etc.) and catalytic conversion processes (UOP, Hawaii Gas). However, due to the proprietary nature of these processes, there is a general lack of data and detailed process descriptions and evaluations are unavailable. Nonetheless, some of the novel pathway technologies might be a good fit for Hawaii, given its special circumstances of being an island state with tropical climate, limited amount of expansive farmland, large demand for jet fuel and low sulfur fuel oil, etc. Government policies and incentives coupled with market forces and entrepreneurial spirit will ultimately decide on the prospects of any bioenergy company on the mainland and on island states in particular.

Table 2.12. A selection of bioenergy companies, their technology, product and status with respect to commercialization (status codes: L=lab scale, P=pilot scale, D=demonstration scale, C=commercial scale)

	Company	Web site	Technology	Product	Status
1.	Coskata	www.coskata.com/	Biomass gasification with microbial conversion of syngas	Ethanol	D
2	Sapphire Energy	www.sapphireenergy.com/	Photosynthetic micro-organisms	Green crude/green gasoline	L
3	Virent Energy Systems	www.virent.com	Aqueous phase reforming of sugars or fiber through catalytic conversion and subsequent conventional refining	Drop-in fuels, chemicals	L
4	POET	www.poetenergy.com	Hydrolysis and fermentation of corn	Ethanol	D
6	Solazyme	www.solazyme.com	Autotrophic conversion of sugars by algae	Fuels, chemicals, high value products	D
7	Amyris Biotechnologies	www.amyris.com	Conversion of plant sugars using engineered micro-organisms (yeast)	Drop-in fuels, high valued products	D
8	Mascoma	www.mascoma.com	Yeast with built-in enzymatic capabilities to hydrolyze starches and cellulose	Ethanol	C
9	Dupont Danisco Cellulosic Ethanol	www.ddce.com	Alkaline pretreatment of lignocellulosic biomass, enzymatic hydrolysis, fermentation	Ethanol	D
10	ZeaChem	www.zeachem.com	Biochemical production of ethyl acetate, lignin gasification to produce hydrogen; ethyl acetate + hydrogen to produce ethanol	Ethanol and other chemicals	D
11	Aquaflow	www.aquaflowgroup.com	Mobile algae harvester	Algae concentrate	D
12	Bluefire Ethanol	www.bfreinc.com	Concentrated acid hydrolysis of lignocellulosic biomass	Ethanol	D
13	Petrobras	www2.petrobras.com.br/ingles/	Veg. oil and animal fat and oil seed for biodiesel, fermentation of sugarcane for ethanol	Biodiesel and Ethanol	C
14	Cobalt Biofuels	www.cobaltbiofuels.com/	Fermentation of various feedstocks	Biobutanol	L
15	Iogen	www.iogen.ca	Steam explosion of lignocellulosic biomass, enzymatic hydrolysis, fermentation	Ethanol	D
16	Abengoa Energy	www.abengoabioenergy.com/corp/web/es/index.html	Lignocellulosic conversion through enzymatic hydrolysis	Ethanol	D
17	Blue Sugars	www.bluesugars.com	Lignocellulosic conversion through dilute acid pretreatment and enzymatic hydrolysis	Ethanol	D
18	LS9	www.ls9.com/	Microbial conversion of plant sugars and glycerin using engineered microorganism	Fuels, chemicals	L
19	Raven Biofuels	www.ravenbiofuels.com/	Lignocellulosic conversion through two stage dilute acid treatment to separate five/six carbon sugars and	Ethanol and furfural	L

	Company	Web site	Technology	Product	Status
			enzymatic hydrolysis		
20	Gevo	www.gevo.com/	Retrofitting existing EtOH plants to produce iso-butanol	Iso-butanol	C
21	Aurora Biofuels	www.aurorabiofuels.com/	Algae	Biodiesel	D
22	Algenol	www.algenolbiofuels.com/	Algae	Ethanol	D
23	SEKAB	www.sekab.com/	Cellulose to ethanol	Ethanol, chemicals	P
24	OriginOil	www.originoil.com/	Using electromagnetic waves to fracture and lyse algae	Algae concentrate with 10% solids	D
25	Propel Fuels	www.propelfuels.com/content/	Fuel stations in CA	Biodiesel and E85	C
26	GEM Biofuels	www.gembiofuels.com/	Supply <i>Jatropha</i> -based feedstock		D/C
27	Lake Erie Biofuels	www.lakeeriebiofuels.com/	Transesterification and acid esterification	Biodiesel 45 Million gallons/yr	C
28	Cavitation Technologies	www.cavitationtechnologies.com/	Produce biodiesel with flow-trough nano-cavitation technology	Sell turnkey conversion systems	C
29	UOP	www.uop.com	Hydrotreating of fats and oils	Green diesel, green jet fuel	D
30	The Gas Company	http://www.hawaiigas.com/	Thermal cracking of oils/fats	Natural gas, renewable hydrogen	D

2.4 Thermochemical Conversion Platform

The primary technologies for thermochemical conversion of biomass include pyrolysis, gasification and combustion. These three main technologies are primary conversion platforms for heat, electricity and liquid fuel production, etc., as shown in Figure 2.22. Individually, each technology has requirements for fuel preparation (processing) and these, along with the technology descriptions, are presented below.

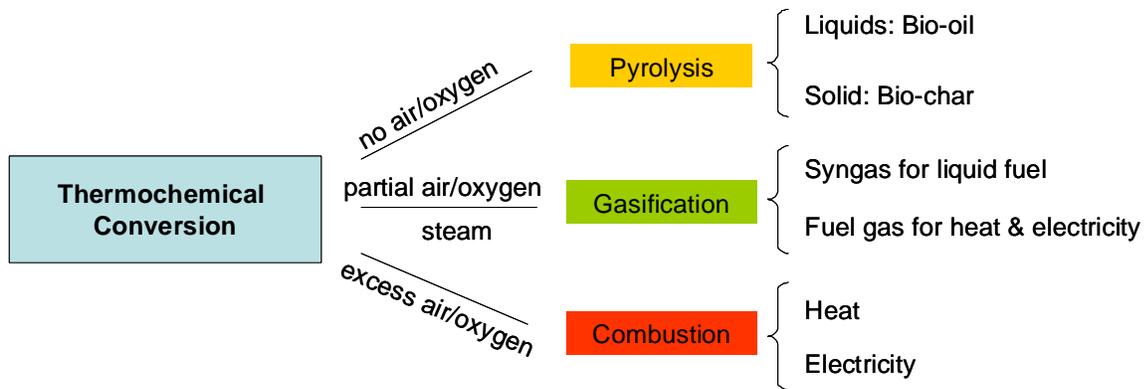


Figure 2.22. The primary thermochemical conversion routes of biomass with different product outputs

2.4.1 Fuel Processing for Thermochemical Platforms

In this module, harvested biomass is reduced in particle size and dried before entering a thermochemical conversion reactor, e.g., gasifier, pyrolyzer or boiler. Four types of unit operation for fuel improvement are described in the following sub-sections (U refers to unit operations and M to modules): U1: milling & drying; U2: pelletization; U3: torrefaction; and U4: torrefaction combined with pelletization.

U1: Milling & drying

Depending on the method of thermochemical conversion, freshly harvested biomass must be reduced in particle size and dried from its as-received state to approximately 6 to 15% moisture.

Size reduction

The biomass feedstock often requires chopping, milling, grinding or pulverization to meet the requirements of the conversion process. The energetic input for size reduction depends largely on the biomass character. Total energy required for whole-tree (freshly harvested) chipping is ~92 kJ/kg. For tub-grinding of agricultural crop residues, the energy requirement range from ~100 kJ/kg (dry basis) for wheat straw with 10 wt% moisture content to ~650 kJ/kg for green forest slash with a content of 32 wt% moisture (19.1 mm screen size) [20].

Two types of milling equipment were compared for the power consumption required to achieve different particle sizes as shown in Table 2.13 [65]. The energy consumption ranges from 0.014 to 0.06 kW_e/kW_{th(wood)} or 252 to 1,080 kJ for 1 kg biomass (for wood with a high heating value of 18 MJ/kg) depending on the equipment and desired particle size.

*Table 2.13. Comparison of power consumption in cutter and vibration milling of wood [65]
(Adapted from reference [65] and assuming 18 MJ/kg of HHV for wood)*

Type of mill	Final average size, mm	Estimated power consumption, kW _e /kW _{th}	Estimated energy consumption, MJ/kg, biomass
Vibration mill	0.035	0.06	1.08
Vibration mill	0.2	0.03	0.54
Cutter mill	0.2	0.055	0.99
Cutter mill	1	0.014	0.252

Size reduction practices used for pyrolysis and gasification are similar. The particle size required for biomass pyrolysis is dependent on the reactor type and target product (i.e. fuel-gas, bio-oil, or char). In general, biomass particle sizes of 1 to 3 mm are typically used for bio-oil production. Entrained flow gasification processes require particles <1 mm. For both of these processes, relatively small particle sizes are required to overcome the poor thermal conductivity of biomass

[1, 3, 66]. If the target product is char (charcoal or bio-char) then particle sizes larger than 5 cm are typically used [67].

Moisture removal

Biomass is dried to meet feeding system and reactor requirements. Power consumption and dryer selection depend on the moisture content of the biomass and its particle size. The three typical choices for drying systems are rotary dryer, flash dryer and superheated steam dryer (SSD). Rotary dryers are least sensitive to the materials size and are the most common, but they also present the greatest fire hazard. Flash dryers are more compact and easier to control, but require a small particle size. SSDs are less common than the other methods and provide significant energy savings. Table 2.14 lists advantages and disadvantages of five types of dryer.

Table 2.14. Summary of the advantages and disadvantages of dryer technologies [68]

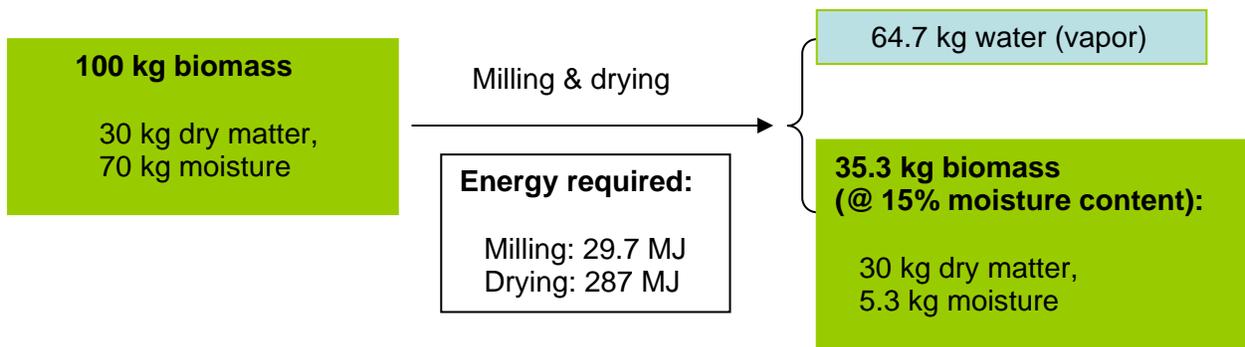
Dryer type	Requires small material?	Requires uniform size?	Ease of heat recovery	Fire hazard	Steam use
Rotary dryer	No	No	Difficult	High	Yes
Flash dryer	Yes	No	Difficult	Medium	None
Disk dryer	No	No	Easy	Low	Yes
Cascade dryer	No	Yes	Difficult	Medium	None
Superheated steam dryer	Yes	No	Easy	Low	Yes

Biomass materials can be heated either directly or indirectly with heat delivered from hot air, combustion products or steam. The wet materials contact with the hot fluid when using direct heating and with a heat exchange surface when using indirect heating. As the water vapor is not diluted with air in the indirect drying process, the evaporated water is easier to condense and recover. Heat recovery may improve system efficiency but at additional capital cost. A heat requirement of 3,500 to 4,700 kJ/kg of water removed is assumed for each dryer in the mass and energy flow calculation [68]. Drying is sometimes achieved by recycling surplus, low-grade heat from the process and this may reduce or remove requirements for additional utility energy [5].

Compared to biomass gasification, the ideal moisture content for fast-pyrolysis targeting the production of bio-oil is typically less than 10 wt% (often 7 wt%). This is slightly lower than for

gasification processes due to the detrimental effect of water on bio-oil properties and the pyrolysis process in general [5]. When the target product from pyrolysis is char (bio-char / charcoal), higher moisture contents can be used (up to ~40 wt%), often with no adverse effects, depending on the reactor type [67, 69].

Figure 2.23 presents mass and energy balances for milling and drying of 100 kg fresh biomass (assuming 70% as-received moisture content) to achieve the final biomass fuel with 15% equilibrium moisture content and a nominal particle size of 0.2 mm. The energy required for milling and drying biomass requires approximately 60% of the energy contained in the starting biomass on the basis shown in Figure 2.23.



Energy for milling required: 990 kJ/kg (dry basis, refer to Table 2.13 for Cutter Miller);
 Energy for drying required: 4,100 kJ/kg for water removal (refers to the average value between 3,500-4,700 kJ/kg [68])

Figure 2.23. Mass and energy flow in the pretreatment (milling and drying)

U2: Pelletization

Pelletization is an extrusion and compression process where biomass is dried, milled/chipped and subjected to high pressure to produce cylindrical pellets. Wood pellets have a higher volumetric energy density and smaller volume than wood chips, making them more efficient to store, transport and process in the biorefinery [3].

Pellet production requires small feedstock particle size (3-20 mm) and moisture content of 10-20 wt%, depending on the pelletization equipment. Pelletization is commonly conducted at a temperature of $\sim 150^{\circ}\text{C}$ [3]. Four steps are typically used in the process: drying, grinding, pelletization and cooling. Only minor improvements in efficiency are expected due to the mature nature of the technology [3].

Biomass pellets usually have an as-received lower heating value ($\text{LHV}_{\text{a.r.}}$) of 16-18 MJ/kg and a bulk density of 650-700 kg/m^3 at a moisture content of 5-10%. The HHV_{dry} is roughly 18-20 MJ/kg [3]. The net fuel-based efficiency is around 94% (i.e. excluding energy required for processing). The gross process-based efficiency is around 87%, i.e. when utility fuel is included (for drying, milling, and cooling). Definition of the efficiency terms is provided in Section 2.4.2.1.1. In newer processes, electricity consumption between 0.025 and 0.045 kWh/kg (input) have been reported, depending on the type of wood [3].

Investment cost range from \$2.5-3.3 million to \$7.4 million for a pelletization plant with pellet production of 24,000 $t_{\text{(pellet)}/\text{y}}$ and 80,000 $t_{\text{(pellet)}/\text{y}}$, respectively [3].

U3: Torrefaction

Torrefaction is a mild pyrolysis process that improves the fuel quality and storage properties of biomass. During the torrefaction process, biomass is dried and lightly decomposed. Torrefaction converts primarily hemi-cellulose to various types of volatiles. The remaining torrefied biomass has a higher carbon content, higher bulk density and much higher energy density than the raw biomass. It is also more brittle and has much better milling properties. A flow diagram of the basic, directly heated, two-stage torrefaction process with gas recycling is shown in Figure 2.24.

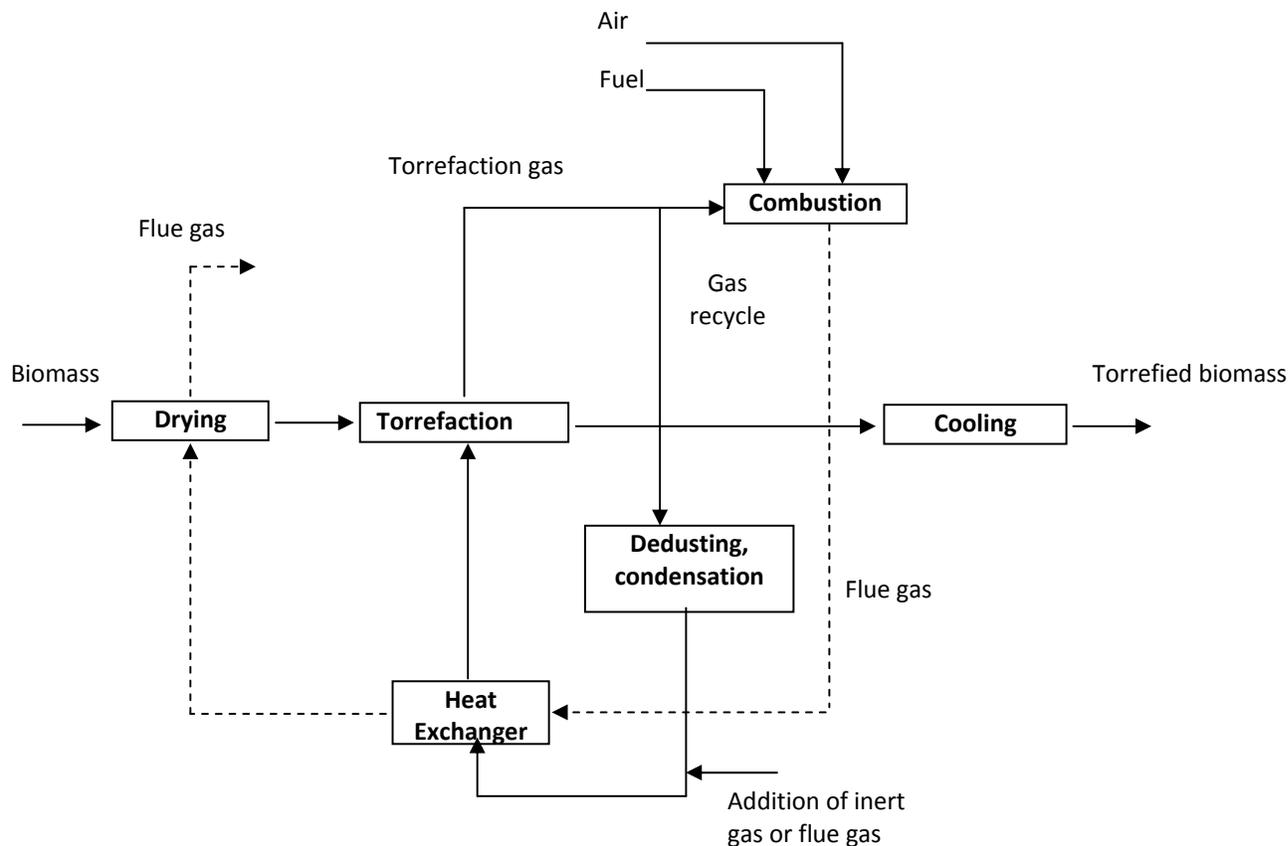


Figure 2.24. Basic concept for directly heated, two-stage torrefaction with gas recycling (adapted from references [3, 70])

Reactor types for torrefaction are similar to those for drying of biomass. Rotary kiln and fluidized bed are popular and are operated with either indirect or direct heating processes. Typical torrefaction conditions utilize a temperature range of 200- 300°C at atmospheric pressure in the absence of oxygen. The heat source could be oxygen depleted hot flue gas, CO₂, nitrogen or superheated steam.

Torrefied biomass is typically reported to contain 70 wt% of the dry biomass and 90% of the initial energy content (based on the LHV of dry biomass and dry torrefied biomass) at a reaction temperature of 250°C and reaction time of 30 minutes [71]. The remaining 30 wt% of the dry biomass is converted into torrefaction gas which contains 10% of the initial biomass energy. The values vary depending on the reaction temperature and time. At higher temperatures and

prolonged reaction times, the feedstock will lose more mass and energy according to [3, 71, 72] (cf. Table 2.15). The main component in the torrefaction gas is steam, which accounts for >75 wt% of its mass when the biomass feedstock has 10 wt% moisture content. Torrefied biomass has a moisture content of 1-6 wt% and is a hydrophobic material, i.e. additional moisture uptake is very low [72].

The heating value of torrefied biomass is typically in the range of 18-23 MJ/kg (LHV) or 20-24 MJ/kg (HHV), and about 5-25% higher than that of the starting dry biomass (17-19 MJ/kg LHV), cf. Table 2.15 [3, 71, 72]. The bulk density of torrefied biomass is typically 180-300 kg/m³ and the corresponding energy density is about 5.5 GJ/m³ [3]. Approximate heating values for torrefied wood, freshly harvested biomass and other forms of biomass pretreatment discussed in this report are shown in Table 2.19, Section 2.4.2. Bulk densities and energy densities are presented in Table 2.23, Section 2.4.2.1.7.

Compared to untreated biomass, size reduction of torrefied biomass requires 85% less energy. For example, the energy required to reduce particles to 100 µm decreases from 0.08 kW_e/kW_{th(dry)} to 0.01-0.02 kW_e/kW_{th} for torrefied biomass [3, 72]. The grinding energy for biomass torrefied at 300°C has been reported to be as low as 24 kWh/t and grinding energy decreases linearly with increasing torrefaction temperature [72].

Torrefaction technology is not yet commercially available. Pechiney built the first demonstration unit in 1987 with a capacity of 12,000 t/y torrefied wood output. However, the design did not lend itself for scale-up [3]. The Energy Center of the Netherlands (ECN) has recently developed a self-sustaining process where the off-gas (torrefaction gas) is reported to provide almost all the process heat requirements [3]. A number of other research groups are also active and further details can be found in a recent review article [72].

Information regarding the energy and mass balance for torrefaction is sparse and, when reported, is often inconsistent or presented ambiguously [3, 71, 72]. For example, the energy balance provided in reference [3] shows significantly more energy in the products than in the starting material. The most recently reported energy and mass balances were provided in a review article from 2011 [72] which uses data from 2006 [71] based on laboratory scale experiments performed

under two sets of typical conditions. Selected information and derived data from [71] is shown in Table 2.15 to provide an estimate of efficiencies under different reaction conditions.

Table 2.15. Mass and energy data for torrefaction of wood

(reported on a dry and moist basis for LHVs and HHVs, adapted from reference [71])

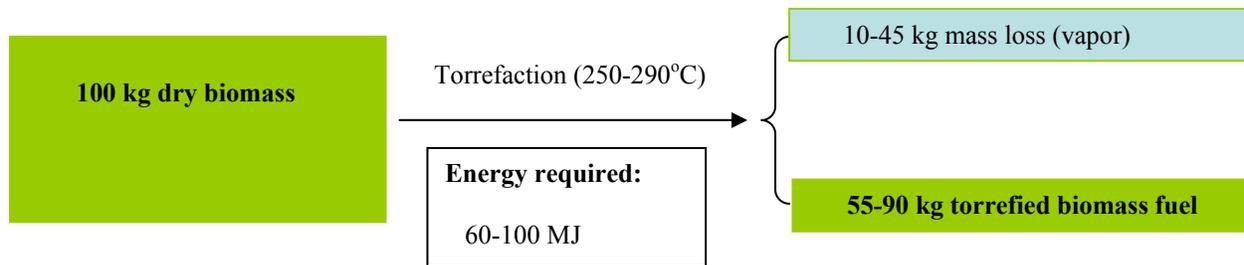
Reaction conditions		Feedstock				Product (dry basis)			Net efficiency, fuel-basis	
Temp, °C	Time, min	Mass, kg	Moisture content, %	LHV _{a,r} , MJ/kg	HHV _{a,r} , MJ/kg	Mass, kg	LHV MJ/kg	HHV MJ/kg	LHV _{a,r} , %	HHV _{a,r} , %
250	30	1.0	0	17.6	18.9	0.87	19.4	20.6	96	95
300	10	1.0	0	17.6	18.9	0.67	21.0	22.2	80	79
250	30	1.0	10.0	15.7	17.0	0.78	19.4	20.6	97	95
300	10	1.0	10.0	15.7	17.0	0.60	21.0	22.2	81	79

The assumptions used to derive the efficiencies are as follows:

1. When the starting biomass had 10 wt% moisture content, all the moisture ends up in the torrefaction gas.
2. In all cases the torrefied wood was assumed to contain zero moisture.
3. If it is assumed that the only product from the process is torrefied wood with 0 wt% moisture content, and all the torrefaction gas is consumed to provide the energy requirements of the process, then:
Net Efficiency = Gross Efficiency (as defined in Section 2.4.2.1.1).
4. If no other energy is required for the plants operation, and assuming no losses, then:
Fuel-based Efficiency = Process-based Efficiency (as defined in Section 2.4.2.1.1)

The data reported in reference [71] on a dry basis (0 wt% moisture content) using LHVs was recalculated to a HHV basis and a starting moisture content of 10 wt% in the biomass feedstock (i.e. the moisture content of the biomass used in their experiments). This information was then used to estimate the net fuel-based efficiency (as defined in Section 2.4.2.1.1) on a dry and moist basis in terms of HHV and LHV, as shown in Table 2.15.

For comparison, the flow of mass and energy were estimated based on the data reported in reference [65]. In this study, reed canary grass, wheat straw, and willow wood were torrefied at three different temperatures (250, 270, and 290°C) and the torrefaction time was set to 30 minutes (laboratory scale), as shown in Figure 2.25.



Assumptions:

1. 0.6-1 MJ/kg (based on energetic balance of the overall process and products in HHV terms) is required for torrefaction process, which is roughly 5% of the original energy (HHV: 18 MJ/kg);
2. Mass yield (wt%) is on the range of 55-90% for three types of biomass fuels (reed canary grass, wheat straw, and willow wood).

Figure 2.25. Mass and energy flow for the torrefaction pretreatment process

Elsewhere, values of 96% have been reported for the net fuel-based efficiency (not accounting for energy required for processing) and 91% for net process-based efficiency (including all energy required for processing, as defined in Section 2.4.2.1.1) [3]. These values match those shown in Table 2.15 for mild experimental conditions (250°C, 30 minutes reaction time). A recent torrefaction review article reported that for a commercial operation, the gross process-based efficiency is unlikely to exceed 80% [72]. It was also stated that the higher the moisture content in the starting biomass, the lower the gross process-based efficiency will be and vice versa [72]. Further work is required to obtain clear information regarding the mass and energy balance for torrefaction at larger-scales.

An economic assessment based on capital investment and production cost estimates using detailed design calculations and vendor quotes was reported by [3]. The maximum capacity of a single torrefaction unit was estimated to be 60,000 t/y torrefied biomass output, corresponding to 40 MW_{th} output (LHV_(dry) of 20 MJ/kg torrefied wood output). This equates to an output of about 170 t/d torrefied wood for an input of 240 t/d wood with 10 wt% moisture content (88,000 t/y input) with a conversion of 72% by dry mass. Capital investments for this size of plant were reported to be \$6.5-9.4 million. Approximately 39% of the cost is installation whereas equipment accounts for ~31%. A zero feedstock cost resulted in a torrefied biomass product cost of \$50-75 /t.

U4: Torrefaction Combined with Pelletization (TOP)

ECN has been exploring the idea of torrefaction combined with pelletization (TOP) to further increase the energy density, storability and transportability of biomass resources [3, 72]. The energy density of TOP biomass can approach 18 GJ/m³ (15-18 GJ/m³ typical) compared to 4.5-5.5 GJ/m³ for torrefied biomass. This is lower than coal (20-29 GJ/m³) but is at least 20% higher than commercial wood pellets (7.8-10.5 GJ/m³) [3, 72, 73].

The energy required to pelletize torrefied biomass is roughly half that of raw biomass [3]. The power required for size reduction for pelletization is reduced by 70-90% when compared to conventional biomass. The properties of TOP, torrefied biomass, wood pellets and wood are shown in Table 2.16.

Table 2.16. Properties of wood, torrefied biomass, wood pellets and TOP; for wood pellets and TOP two sets of values are given to show the influence of different moisture contents (reproduced from reference [72])

Properties	Unit	Wood	Torrefied biomass	Wood pellets		TOP pellets	
Moisture	wt%	35	3	10	7	5	1
LHV (as-received)	MJ/kg	10.5	19.9	15.6	16.2	19.9	21.6
LHV (dry)	MJ/kg	17.7	20.4	17.7	17.7	20.4	22.7
Energy density	GJ/m ³	5.8	4.6	7.8	10.5	14.9	18.4

Summary of Biomass Pretreatment Technologies

It can be seen from the information provided in this section that pre-treatment of biomass has benefits over untreated biomass in terms of improved energy density, heating value, transportability and storability. This does, however, incur an increase in capital and production costs. A technical and economic comparison of these pre-treatment technologies with fast-pyrolysis is provided in Section 2.4.2.1.7. The different types of fast-pyrolysis reactors, upgrading methods and applications for bio-oil are described in Sections 2.4.2 – 2.4.2.1.6.

2.4.2 Pyrolysis Platform (pyrolysis oil and char)

Pyrolysis is a highly versatile thermal decomposition process that converts organic or fossil matter in the absence of oxygen into three phases: a condensed liquid (pyrolysis oil or tar), solid residue (char) and non-condensable gas (fuel-gas). Their relative proportions depend on the feedstock, pyrolysis mode, reactor type and reaction conditions [1, 66, 74, 75]. Table 2.17 summarizes typical product distributions from the main modes of biomass pyrolysis, alongside torrefaction and gasification for comparison. Table 2.18 gives a more detailed breakdown of biomass pyrolysis technologies in terms of reaction conditions and products. All three products from pyrolysis are energy carriers. Char has the highest energy density (MJ/kg) followed by oil, and gas the lowest (cf. Table 2.19).

The energy densification of biomass via pyrolysis to generate pyrolysis oil (bio-oil) and char is particularly attractive for storage and transportation of biomass resources from surrounding regions to centralized locations for processing or upgrading. The fuel-gas generated during fast-pyrolysis for bio-oil production is usually combusted to provide heat required to sustain the process, or for other local heat requirements such as biomass drying. Table 2.19 compares typical heating values, moisture content as well as mass and energy balances of freshly harvested biomass with torrefaction, pelletization and fast pyrolysis.

The waste products from a fully integrated biomass pyrolysis process are CO₂, H₂O (flue gas), and ash when the char is combusted as part of the process. If the char is exported, the ash is contained within the char.

Section 2.4.2.1 summarizes technologies and processes for maximizing the bio-oil yield from biomass and Section 2.4.2.2 outlines those optimized for char production.

Table 2.17. Typical product weight yields (dry wood basis) obtained by different modes of pyrolysis and gasification, adapted from [1, 66]

Mode	Conditions	Solid	Liquid	Gas
Fast (rapid/flash) pyrolysis	500-1000°C, hot vapor residence time ~1 s	12% Char	75%	13%
Intermediate pyrolysis	~500°C, hot vapor residence time ~10-30 s	25% Char	50% in 2 phases*	25%
Conventional pyrolysis (carbonization/slow)	~400°C, vapor residence time, hours/days	35% Char	30%	35%
Torrefaction	~290°C, solids residence time ~ 10-60 min	70-90%	0-5%	10-25%
Gasification	~750-900°C, hot vapor residence time ~1 s	10% Char	5%	85%

* 2 phases refers to a aqueous and organic phase

Table 2.18. Biomass pyrolysis technologies, reaction conditions and products, reproduced from [5]

Mode	Residence time	Temperature (°C)	Heating rate	Major products
Conventional carbonization	hours-days	300-500	very low	char
Pressurized carbonization	15 min – 2 h	450	medium	char
Conventional pyrolysis	hours-days	400-600	low	char, liquids, gases
	5 – 30 min	700-900	medium	char, gases
Flash pyrolysis	0.1 – 2 s	400-650	high	liquids
	<1 s	650-900	high	liquids, gases
	<1 s	1,000-3,000	very high	gases
Vacuum pyrolysis	2 – 30 s	350-450	medium	liquids
Pressurized hydrolysis	<10 s	<500	high	liquids

Table 2.19. Approximate heating values, mass and energy balances for biomass and pretreated biomass (using data from [1, 3, 5, 66, 72, 76])

Properties	Moisture content	Heating value		Balances	
		LHV _{ar}	HHV _{dry}	Mass ^A	Energy ^B
Units	Wt%	MJ/kg	MJ/kg	%	%
Fresh biomass	50-60	6-9	15-20	100	100
Pelletized biomass	5-10	13-18	15-20	~95	~94
Torrefied biomass	2-6	~18-21	~19-22	70-90	~82
Torr & pelletized (TOP)	1-5	~18-21	~19-22	~65-85	~80
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 on a dry basis

^B 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

2.4.2.1 Pyrolysis for Bio-oil Production

In this section, thermochemical processes that are used for producing bio-oil from biomass are presented. Before discussing these processes, the terminology used to compare bio-oils and processes are described and defined.

2.4.2.1.1 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 CO₂ and H₂O products; H₂O in liquid phase (heat of condensation recovered)
- 2) Lower heating value (LHV) – heat released by complete combustion of fuel to CO₂ and H₂O products; H₂O 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 [20]:

$$\text{HHV}_{\text{a.r}} = (1 - M_{\text{wb}}) * \text{HHV}_{\text{dry}} \quad (2.4)$$

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 2.5 [20]:

$$\text{LHV} = (1 - M_{\text{wb}}) \{ \text{HHV}_{\text{dry}} - \lambda(M_{\text{db}} + 9H) \} \quad (2.5)$$

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 [20].

However, it is important to note that bio-oils are 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}) [20, 77]. 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 fast-pyrolysis reactors (and 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 [5]”. Elsewhere ‘thermal efficiency’ has been defined in the same manner on an LHV_{a.r} basis [3]. 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} [3] and elsewhere on a HHV basis [5]. 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. In cases where the basis of the efficiency was not given in the cited literature source it will be indicated in the text.

$$\begin{aligned} \text{Net thermal efficiency}_{\text{fuel-basis}} (\text{Eff}_{\text{N-FB}}) \\ = \text{energy in bio-oil} / \text{energy in biomass} \end{aligned} \quad (2.6)$$

$$\begin{aligned} \text{Gross thermal efficiency}_{\text{fuel-basis}} (\text{Eff}_{\text{G-FB}}) \\ = (\text{energy in bio-oil} + \text{useful energy products}) / \text{energy in biomass} \end{aligned} \quad (2.7)$$

$$\begin{aligned} \text{Net thermal efficiency}_{\text{process-basis}} (\text{Eff}_{\text{N-PB}}) \\ = \text{energy in bio-oil} / (\text{energy in biomass} + \text{auxiliary energy input}) \end{aligned} \quad (2.8)$$

$$\begin{aligned} \text{Gross thermal efficiency}_{\text{process-basis}} (\text{Eff}_{\text{G-PB}}) \\ = (\text{energy in bio-oil} + \text{useful energy products}) / (\text{energy in biomass} + \text{auxiliary} \\ \text{energy input}) \end{aligned} \quad (2.9)$$

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

Note: Detailed information regarding energy balances for fast-pyrolysis processes are often proprietary. Energy balances 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% [1, 4, 66, 78-80]. 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 in Section 2.4.2.1.3).

In light of these issues, individual mass and energy balances cannot be justified for each type of fast-pyrolysis reactor discussed later (Section 2.4.2.1.3). Instead, the following generic efficiencies are considered a reasonable estimate for all the fast-pyrolysis systems discussed herein:

Net thermal efficiency_{fuel-basis} \approx 65% based on LHV_{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_{dry}, the Eff_{N-FB} is approximately 75%.

Net thermal efficiency_{process-basis} \approx 60% on a LHV_{a,r} basis (same M.C. as above) and 70% on a HHV_{dry} basis.

In both cases only the 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. Efficiencies of fast-pyrolysis reactors are addressed in the summary at the end of Section 2.4.2.1.3.

2.4.2.1.2 Introduction to fast-pyrolysis

To optimize the liquid yield (bio-oil) from biomass pyrolysis the following conditions are typically used: rapid heating rates (>400 °C/s), medium temperature (450-550 °C), short hot vapor 'residence time' (RT, <3 seconds) and atmospheric pressure. These conditions generally results in a product distribution of 10-20 wt% char, 65-75 wt% bio-oil and 10-25 wt% fuel-gas with respect to the dry biomass feedstock [1, 66, 75]. This type of pyrolysis is widely known as 'fast-pyrolysis'. However, the term is often used interchangeable with flash or rapid pyrolysis; although there are subtle differences between process conditions in each case (cf. Tables 2.17 and 2.18). In this report these three processes are grouped under the umbrella term 'fast-pyrolysis' which is defined here as a heating rate greater than 400 °C/s and a hot vapor residence

time (RT) of <3 seconds. In general, only fast-pyrolysis processes are considered viable for producing bio-oil on a commercial-scale [1, 3, 66]. It should be noted that slight changes in the biomass feedstock or reaction conditions results in bio-oils with different properties. The influence of the reaction temperature on the products from fast-pyrolysis is shown alongside those for gasification in Table 2.20.

Table 2.20. Yield and oxygen content of bio-oils from different operating conditions, reproduced from [74]

Mode	Temperature range	Liquid product	Gas products	Char
Fast-pyrolysis	450-500°C	Maximum (high oxygen content) ↑	Minimum ↓	Low-Medium (high oxygen content) ↑
	600-650°C			
Steam gasification	700-800°C	Minimum (low oxygen content)	Maximum	Low (low oxygen content)
	900-1000°C			

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 M.C. 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 [1, 5] (further details are given in the Section 2.4.2.1.4).

Bio-oil is a brown liquid with approximately the same ratio of carbon, hydrogen, oxygen and nitrogen as the parent biomass. Bio-oil accounts for approximately 65-75 wt% of the starting dry biomass [1, 66, 76]. The bio-oil contains approximately 65% of the energy in the ‘as-received’ starting biomass based on $LHV_{a,r}$, and a feedstock moisture content and bio-oil moisture content of 7% and 22%, respectively. When based on the HHV of dry biomass, a 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%) [74]. The yield of bio-oil is approximately 550-625 L/t assuming a mass conversion of 65-75% from the dry biomass feedstock and a bio-oil density of 1.2 kg/L [74].

The char from fast-pyrolysis is a black-brown, dry, brittle solid which contains very little water, <5 wt% [1]. 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 [1, 5, 66]. Further details regarding chars derived from biomass pyrolysis are given in Section 2.4.2.2.

Pyrolysis fuel-gas has a similar composition as syngas from gasification (mainly CH₄, CO, CO₂ and H₂) 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) [1, 66]. Table 2.19 summarizes the approximate heating values (LHV_{a,r} and HHV_{dry}) of harvested biomass (M.C. 50-60 wt%) and the products from fast-pyrolysis, torrefaction and pelletization along with typical mass and energy balances.

Overview of Uses for Bio-oils

Bio-oil has been demonstrated to be suitable for direct use in boiler and stationary engine applications (combustion processes) for power generation (electricity, heat, or combined heat and power - CHP) and, with less success, in turbine platforms [1, 66, 81, 82]. It should be noted, that some form of upgrading is often required before bio-oils can be combusted. These include filtration to remove char and ash, and/or the use of additives to avoid ageing of the bio-oil or to reduce its corrosiveness or harmful combustion emissions (discussed further in Section 2.4.2.1.4, Upgrading) [1, 5]. The properties of bio-oil are also sensitive to the reactor type, reaction conditions and changes in the feedstock.

Due to bio-oil's lower energy density and higher oxygen content compared to petroleum derived fuels (Table 2.21), upgrading is also required before it can be used as replacement transportation fuel. Upgrading, however, has yet to be proven on a commercial-scale. Bio-oil can also be used as feedstock for gasification-Fischer-Tropsch processes to produce biofuels (H₂, methane-SNG, gasoline, diesel and jet-fuel) and chemicals. However, only limited tests have been reported [1, 5, 66]. Upgrading of bio-oil to biofuels is discussed further in Section 2.4.2.1.4

Table 2.21. The properties of wood derived bio-oil, petroleum derived heavy fuel oil and No.2 diesel, adapted from [66, 74]

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*	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

n/a, not applicable

** 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.*

Process Routes for Bio-oil

There are several process routes that can be used to produce fuels/chemicals or power from biomass fast-pyrolysis. Typically, a pyrolysis platform for bio-oil production consists of 3-5 primary modules depending on the process route considered:

- 1) Pretreatment, including milling and drying (M_{pr});
- 2) Pyrolyzer, including recovery and storage (M_{py});

- 3) Transportation (T);
- 4) *Optional* Upgrading, to produce mixed transportation fuels and chemicals (M_{up});
- 5) *Optional* Refining, after upgrading the mixed product needs to be refined (M_{rf});
- 6) Application, generate heat, power or electricity; or if upgraded, transportation fuels or chemicals (M_{ap}).

Three possible processing routes can be summarized as follows (but not limited to):

- i) where the bio-oil is produced and used directly as a fuel:

$$M_{pr} \rightarrow M_{py} \rightarrow T \rightarrow M_{ap} \text{ (combustion or gasification)}$$

- ii) where the bio-oil is produced and then upgraded centrally before being refined and used as fuel and chemicals:

$$M_{pr} \rightarrow M_{py} \rightarrow T \rightarrow M_{up} \text{ (central)} \rightarrow M_{rf} \rightarrow M_{ap} \text{ (transportation fuels/chemicals.)}$$

- iii) where the bio-oil is produced and upgraded locally before being refined centrally for use as fuel and chemicals:

$$M_{pr} \rightarrow M_{py} \rightarrow M_{up} \text{ (local)} \rightarrow T \rightarrow M_{rf} \text{ (central)} \rightarrow M_{ap} \text{ (transportation fuels/chemicals.)}$$

In a bio-refinery concept many possible combinations of these platforms and routes can be envisaged, some of these are discussed in the latter sections (Section 2.4.2.1.6 and Section 3).

2.4.2.1.3 Pyrolysis module (M_{py})

A pyrolysis process module (M_{py}) includes a number of different unit operations that are dependent on the reactor type. A brief description of the fundamentals of biomass pyrolysis is given followed by descriptions of the most common unit operations and reactor types for bio-oil production via fast-pyrolysis.

When biomass is heated in an oxygen free environment (pyrolysis) many parallel sets of sequential reactions occur which include dehydration, cracking (covalent bond cleavage), isomerisation, dehydrogenation, aromatization, coking, condensation and rearrangement [74, 75]. This complex process results in fuel-gas, bio-oil and char which may further interact with one-another to form new intermediates and final products. The final product distribution and composition of the products are highly dependent of the reactor type, reactor geometry and operating conditions such as temperature, vapor residence time at elevated temperature, and pressure [75, 83]. 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 [1, 2, 5]. In practice the bio-oil is rarely recovered completely free of ash and char.

Pyrolysis consists of several distinct processes as listed above. Independent of the specific process or reactor type, the primary reaction mechanism is cracking (covalent bond cleavage in large molecules resulting in smaller molecules) followed by secondary recombination / polymerization reactions. A diagram showing this complex process is presented in Figure 2.26.

Only transport and circulating fluidized-bed pyrolysis reactors have been commercialized for the production of food flavorings from biomass [1, 66]. 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. Three types of pyrolysis reactor that are potentially suitable for commercial bio-oil production have been operated / tested at demonstration scale (~10-200 t/d, input dry biomass): 1) fluidized-bed, 2) rotating cone, 3) ablative [1, 66]. These three reactor types are described in sub-section U2.

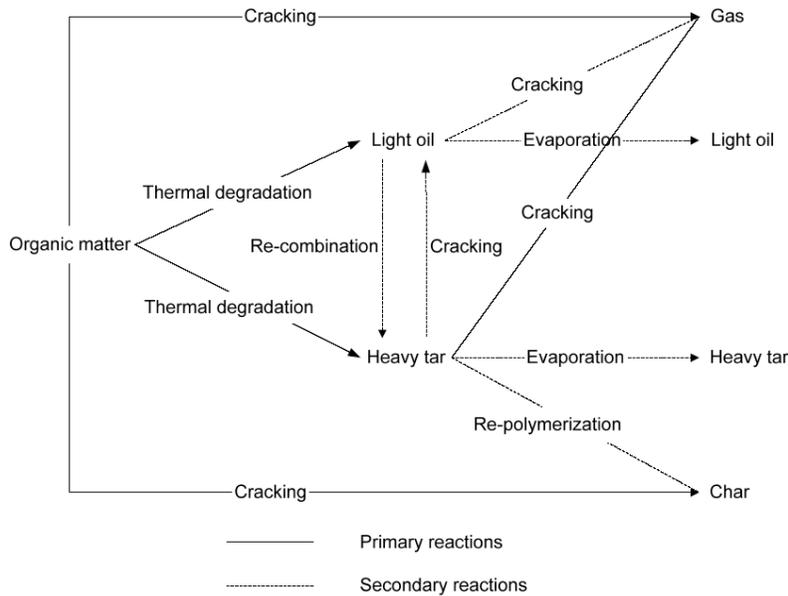


Figure 2.26. Diagram of primary and secondary pyrolysis reactions, reproduced from [74]

U1: Inert gas requirement

Fluidized-bed pyrolysis reactors require an inert gas as fluidizing agent, and rotating cone designs needs an inert carrier gas (reactor types are described in the following sub-section). Flue gas from an interconnected or external combustion reactor is typically used to provide heat and an inert environment for the pyrolysis unit. Fuel-gas and char are often used as fuel in the combustor [1, 5].

U2: Fast-pyrolysis reactors

Three types of pyrolysis reactors are thought to be suitable for commercial-scale production of bio-oil. Typical configurations for fluidized-bed reactors are shown in Figures 2.27 and 2.28, whereas Figure 2.29 depicts a rotating cone design and Figure 2.30 summarizes an ablative reactor. The same type of pyrolyzer may be integrated into various processing platforms with different structural configurations and operating conditions. The main features are summarized in the following sub-section.

Pyrolysis is an endothermic process that requires an energy (heat) input to sustain the process. This can be achieved by internal (autothermal) or external (allothermal) heating. The heat can be

generated externally by burning part of the feedstock or pyrolysis products (Figure 2.28) or by burning fossil fuels. Heating is discussed further for each type of reactor in the following sub-sections.

U2-A: Fluidized-bed pyrolyzers

There are two broad types of fluidized-bed (FB) reactors used for fast-pyrolysis of biomass, bubbling and circulating fluidized-beds.

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, 5, 66]. Figure 2.27 shows a typical configuration with a cyclone and ESP to aid the recovery of bio-oil [1]. 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 t/d) [1]. 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 [5]). 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 [1]. The char separation is easier than in circulating FB reactors and can be exported if another heat source is preferred for driving the pyrolysis reactions. 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 [5] as discussed in the summary at the end of this sub-section.

The largest bubbling bed units currently operating or under construction are: 100 t/d and 200 t/d units in Canada (two pilot and two commercial) based on a design by RTI and built by Dynamotive (t/d refers to dry-feedstock input). Biomass Engineering Ltd in the UK is constructing a 6 t/d plant. Fortum built a 12 t/d plant in Finland which has since been dismantled. Metso, working with UPM and VTT in Finland, constructed and operated a 55 t/d unit in Tampere, Finland. Anhui University of Science and Technology in China is overseeing construction of three 14 t/d demonstration plants in China [1].

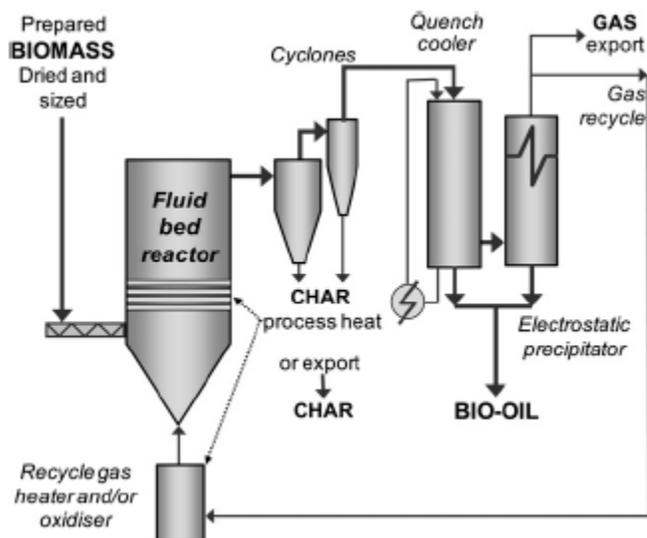


Figure 2.27. Bubbling fluidized-bed pyrolyzer with electrostatic precipitator, reproduced from [1]

Dynamotive currently operates the largest reactors and was contacted to obtain up-to-date information. However, no response was received. A summary of information from the Dynamotive website ([4], accessed August 2012) includes mass and energy balances and limited production cost data. The mass balance for a dry biomass input is 20, 68 and 12 wt% for char, bio-oil and fuel-gas, respectively. The energy content of char and bio-oil is 29.7 MJ/kg and 17.9 MJ/kg, respectively. Note that lower or higher heating value and moisture contents were not specified and the fuel-gas energy content was not reported. Fuel-gas is claimed to be consumed to generate 94% of the plants energy requirements, and all the char and bio-oil are available for export. Dynamotive reports that with a feedstock cost of \$30/t_(dry), bio-oil production costs will be \$1.82/gal. At higher feedstock costs of \$130/t_(dry) bio-oil costs \$3.25/gal are anticipated. The analysis is based on a 400 tonne dry biomass per day plant (i.e. two 200 t/d units) [4]. The bio-oil is described as not suffering from phase separation or polymerization (ageing) upon storage and is said to have been stored for up to 4 years before being successfully upgraded to mixed transportation fuels. One tonne of dry biomass (input to the pyrolyzer) is reported to produce 300 kg of transportation fuels (35% diesel, 35% naphtha, 30% jet-fuel). From their most recent press release (Sept. 2012) the “minimum conversion cost \$/gal total fuel is \$4.55 for replacement gasoline and diesel produced from biomass pyrolysis... projected to reach \$2.32 by 2017 with continued R&D” [4].

Restated, 1 dry tonne of biomass produces 680 kg of bio-oil which can be upgraded to produce 300 kg of transportation fuels (44% conversion by mass of the bio-oil), based on information provided by Dynamotive. Upgrading is described as a two-stage process (reforming and refining) using traditional refinery practices and requires relatively low amounts of hydrogen [4]. Upgrading is achieved via a ‘hydro-reforming’ process where the aqueous phase is separated before hydro-treating the oil phase [4]. This allows for the recovery of acetic acid and methanol (from the aqueous phase) at yields of roughly 5,000 and 3,000 t/y respectively, based on a 200 t/d pyrolyzer. Current values for these two co-products are ~\$400-600/t [4]. The design of the pyrolysis plant is modular (200 t/d units) and is suitable for applications where pyrolysis and upgrading are decoupled [4].

It has been reported in literature that bio-oil produced using Dynamotive’s BioTerm process was tested for direct combustion in a turbine, but continuous operation could not be achieved due to technical problems [81].

VTT (Technical Research Centre of Finland) developed a bubbling FB based fast-pyrolysis process, the ‘integrated pyrolysis concept’ [81]. In this design, the fast-pyrolysis unit is coupled to a biomass CHP installation. Bio-oil is produced as a co-product with all the char and fuel-gas directed to the CHP boiler to minimize losses. The largest scale unit currently operating is a pilot-plant with 7 t/d capacity (dry input). The short term aim for this process is to produce bio-oil for decentralized heating applications (furnaces and kilns) and as a substitute for fuel oil combustion in small to medium scale boilers (electricity generation). This approach has been reported to be technically feasible, while economic viability was assessed to be highly dependent on a low cost biomass feedstock [81]. VTT is also working on other coupled systems which incorporate fast-pyrolysis. Further details can be found elsewhere [1, 84].

Mass and Energy balance for 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. Based on the available information [1, 4, 5, 66], bubbling fluidized-beds typically produce bio-oil yields of 60-75 wt% from woody biomass on a dry-feed basis, which accounts for about 70% in energy terms (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 15-20 wt% and contains about 5-10% of the energy in the starting biomass (basis not reported) [1, 66]. The net thermal efficiency (fuel-basis) is typically reported to be in the order of 60-70% (basis not reported) [1, 5, 66]. No reports for the net or gross thermal efficiency on a 'process-basis' could be found.

Due to the lack of information it is not possible to present a meaningful energy balance that would distinguish this reactor type from the others described below. Therefore, the generic $\text{Eff}_{\text{N-FB}}$ of 65% (as stated in Section 2.4.2.1.1) can be assumed as a reasonable estimate for BFB processes (based on $\text{LHV}_{\text{a,r}}$ and M.C of starting biomass 6-10 wt%). When based on HHV_{dry} the $\text{Eff}_{\text{N-FB}}$ is approximately 75%.

Circulating fluidized-beds (CFB): Circulating fluidized-beds and transport reactors have many of the same elements as BFB described above. A schematic of a typical CFB reactor is shown in Figure 2.28. The main drawback compared to a bubbling bed reactor is that char is more difficult to remove from the bio-oil. However, CFBs have the potential for greater throughput than BFBs and their construction and operation is well understood from the petro- and petro-chemical industry [1, 5, 85]. Envergent Technologies is marketing a commercial unit of 400 t/d [86] compared to the largest bubbling-bed reactors which operate at 200 t/d [1, 4, 81]. 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 [6]. 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 [1, 6, 81].

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 t/d [1] with one unit operating at 400 dry t/d plant in Malaysia. Fifteen pyrolysis plants are planned by 2015 under the Malaysian Premium Renewable Energy's bio-oil project [81]. 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 t/d commercial units [2]. An

alternative CFB fast-pyrolysis process is being developed by Metso and UPM, (Finland) who operate a 10 t/d demonstration unit [1].

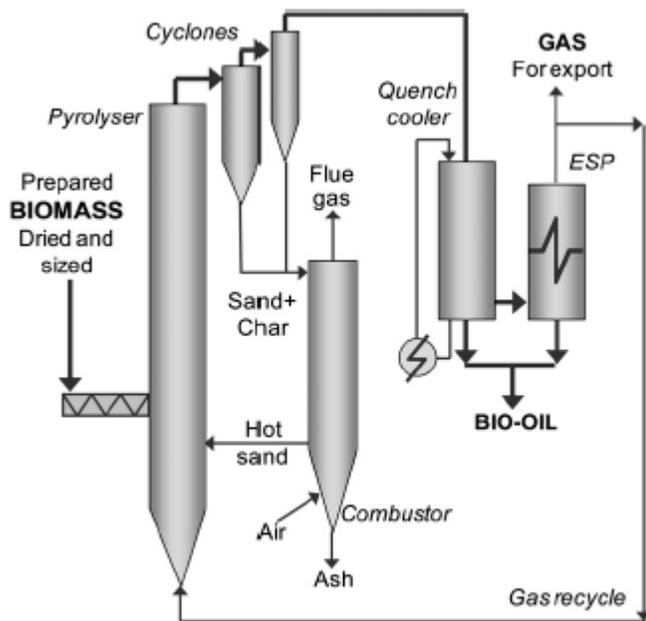


Figure 2.28. Circulating fluidized-bed pyrolyzer with electrostatic precipitator, reproduced from [1]

Summary of UOP LLC process: UOP LLC is constructing a 1 t/d (dry biomass input) pilot scale unit at the Tesoro refinery on Oahu with funding from the DOE [87]. The targeted capacity of the unit is four barrels of RTP green fuel (bio-oil or) per day (~635 L, 760 kg) when a benchmark reference feedstock, a Canadian hardwood, is used [2]. The aim of this pilot plant is to demonstrate the performance of Envergent's RTP™ (Rapid Thermal Processing) unit integrated with UOP's upgrading technology to convert RTP green fuel into drop-in fuel oil and transportation fuels. Furthermore, the influences of different biomass feedstocks, including those available in Hawaii, are to be evaluated. [2].

Through personal communication with a UOP representative [2] the following details were obtained: the mass balance for Envergent's commercial RTP units is 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 [2].

The char is combusted to supply the thermal requirements of the RTP unit. In a commercial system, the fuel-gas may be used to provide process heat (e.g. for drying the biomass feedstock) and/or electricity. Alternatively, the fuel-gas may be available for any other purpose which may best suit the project. The fuel-gas, flue gas, and low-grade waste heat may be exploited to generate electricity at a commercial scale facility. UOP estimates [2] that a 400 t/d (dry input) unit could generate 4-7 MW_e from fuel-gas and waste heat, while the electrical requirement for the whole site would be roughly 5 MW_e (biomass drying and sizing, pyrolysis, and recovery). The cost effectiveness of implementing this in a fully integrated system has not yet been fully evaluated.

UOP indicates that the RTP green fuel (bio-oil) is stable (i.e. it stays within a defined viscosity range) and does not require additives to prevent ageing over the time frame typical of storage (~6 months when properly stored). UOP indicates that RTP green fuel is suitable for direct combustion in boiler applications to generate heat and/or power and is suitable for co-firing with coal or other fossil fuel with appropriate fuel handling modifications. RTP green fuel has been tested as a replacement for fuel oil in a boiler and could be fired at levels up to 100% of the design fossil energy equivalence without derating the facility [2]. Information on the scale, duration and performance of the tests is proprietary. To use the RTP green fuel in diesel generators would require certain equipment modifications and use of additives and does not appear to be a key objective of the project.

UOP plans to upgrade RTP green fuel (bio-oil) to transportation fuels via hydro-processing at low temperature using proprietary catalysts that will require 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 one tonne 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 [2].

The efficiencies for producing RTP green fuel (based on the definitions in Section 2.4.2.1.1) from a 400 t/d unit on a LHV as-received basis with 4-10 wt% and 15-30 wt% moisture in the feedstock and RTP green fuel, respectively, are:

$$\text{Net thermal efficiency}_{\text{fuel-basis}} \cong 65\text{-}70\%,$$

$$\text{Gross thermal efficiency}_{\text{fuel-basis}} \cong 75\text{-}80\%$$

$$\text{Net thermal efficiency}_{\text{process-basis}} \cong 65\text{-}70\%$$

$$\text{Gross thermal efficiency}_{\text{process-basis}} \cong 70\text{-}75\%$$

There is no significant difference in efficiency between the 150 t/d and 400 t/d units. Information regarding the efficiency of UOP's upgrading process is not publically available at present. Likewise, cost data are not available for production of RTP green fuel (bio-oil) or transportation fuels. Capital and operating costs for a commercial unit are also unavailable [2].

Summary of general studies: A number of detailed studies have been reported for techno-economic, design case and life cycle assessments for biomass fast-pyrolysis using a circulating fluidized-bed reactor with upgrading via hydro-processing [6, 85, 88, 89]. Detailed techno-economic information has been reported from a European Union [90] 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 t/d) [85]. The reactors were a CFB (built by Wellman Process Engineering Ltd - WPE) constructed as part of the project and a rotating cone that was already in existence. The CFB reactor has since been decommissioned due to excessive authorization cost under IPPC (Integrated Pollution Prevention and Control) [85] whereas the rotating cone (operated by Biomass Technology Group [78]) is still operational and is discussed later in sub-section U2-B.

A thorough report was published in 2009 detailing a plant design for 2,000 t/d (dry, poplar woodchips input) for fast-pyrolysis followed by hydro-treating and hydro-cracking processes to produce 'drop-in' gasoline and diesel [6]. Detailed heat and material balances, as well as equipment cost estimates were reported. That study was followed by a life cycle assessment in

2011 [89] for the same process. The findings from these studies that are related to costs are summarized in Section 2.4.2.1.7.

It is worth noting that these two independent studies (supported by EU [85] and US [6] [89] 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 hydro-treatment [6, 81, 85, 88, 89]. The most 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 [88] and the latter is an LCA of transportation fuels from biomass pyrolysis [81].

Mass and energy balance: Mass and energy balances as described for the UOP project are generally in accordance with the above mentioned literature on circulating fluidized-bed technologies.

U2-B: 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 [1, 85]. A small amount of inert gas is required to transport hot sand from the combustor to the pyrolyzer. An early prototype of this reactor type is shown to the left of Figure 2.34 with its integration into a fast-pyrolysis module to the right [1]. 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 [1]. On the negative side, the required biomass particle size is smaller than for fluidized-beds, typically 0.2 mm [5]. 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 is available [1, 3, 85].

Rotation cone pyrolyzers were invented at the University of Twente, the Netherlands and Biomass Technology Group (BTG, [78]) of the Netherlands developed the process. A 6 t/d unit is operational and a 50 t/d plant was installed in Malaysia in 2004 to produce bio-oil for co-firing in a stationary diesel engine [1, 81]. A 120 t/d reactor is currently the largest commercially

available unit according to the BTG website, although a 240 t/d unit and larger will be available in the near future (as of Sept. 2012) [78]. Bio-oil from the BTG process has been successfully co-fired in a natural gas combined cycle plant in the Netherlands [81].

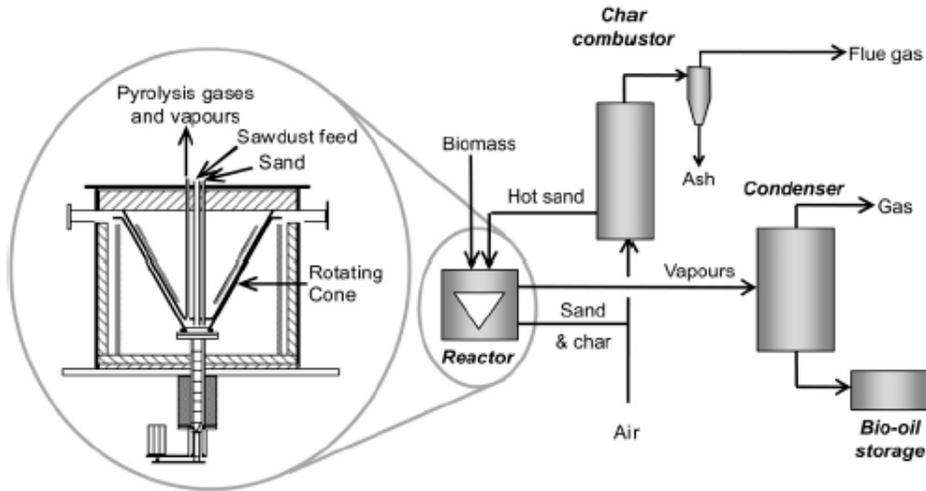


Figure 2.34. Rotating cone pyrolysis reactor, reproduced from [1]

Mass and energy balance: Mass and energy balances have been reported for a typical rotating cone pyrolysis unit ($25 \text{ MW}_{\text{th(input)}}$, $\sim 150 \text{ t/d}$ dry biomass input, $\text{LHV}_{\text{dry}} 14.7 \text{ MJ/kg}$) [3]. Approximate bio-oil yields are 60-70 wt% of the dry-feed, fuel-gas $\sim 20 \text{ wt\%}$ and char $\sim 10 \text{ wt\%}$. The energy contents of the bio-oil, char, and fuel-gas are approximately 66%, 26%, and 8% of the $\text{LHV}_{\text{a,r}}$ 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 [3].

The $\text{Eff}_{\text{N-FB}}$ is stated to be 66% and the $\text{Eff}_{\text{G-PB}}$ as 64% when utility energy is accounted for, based on $\text{LHV}_{\text{a,r}}$ and moisture contents as above [3]. 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 [3].

U2-C: Ablative reactors

Ablative processes are fundamentally different from the other methods of fast-pyrolysis described above as the rate of reaction is *not* limited by the rate of heat transfer through the biomass particle. Heat is transferred from the hot reactor (700 °C) wall under high pressure (30-50 bar) to the biomass. Therefore, larger particle sizes can be used than for fluidized-beds or rotating cone designs [1, 5, 66]. The process can be thought of as melting butter on a hot surface, if the butter is moved across the surface it melts more quickly. In an ablative process, the hot metal surface is moving while the wood is held stationary. The wood melts as a thin film which quickly evaporates. Advantages of this design are that wood boards of 10 x 50 x 350 mm or standard woodchips (60 x 40 x 5 mm) can be fed to the reactor [1, 79, 91]. The exact feeding mechanism is unclear and may involve mixing recycled bio-oil with the feedstock. This way of feeding the reactor is reported to save on the energy required for feedstock pretreatment compared to the other processes outlined above [1, 79, 91].

In addition, no carrier gas is required in this process which translates to smaller capital cost and reduced heat loss. Additionally, bio-oil recovery is easier than in FB or rotating cone reactors. However, scale-up is not well understood and the reactor is mechanically driven and operates at high pressure which makes it more complex than fluidized-bed reactors [1]. Another drawback is that larger amounts of heavy oil (tar) are reported to be produced in ablative reactors compared to other reactor types [5]. A schematic example of an ablative pyrolysis reactor is shown in Figure 2.30.

The ablative design is aimed at small to medium scale applications in remote locations. For example, PYTECH's 6 t/d reactor fits into a standard 40 ft container [79]. PYTECH (north Germany) built a 6 t/d unit in 2006 which is undergoing testing and a 50 t/d plant is being designed (i.e. eight 6 t/d units operating in parallel) [1, 79, 91]. For the 50 t/d plant, roughly a quarter of the bio-oil produced is predicted to be used to fuel two stationary 315 kW_e diesel engines (CHP) for onsite power generation, with the remainder of the bio-oil exported to a customer; i.e. to fuel six CHP diesel engines [79, 91]. The only other examples are laboratory scale units at Aston University (UK), Institute of Engineering Thermophysics (Ukraine), Latvian

State Institute (Latvia) and Technical University of Denmark [1]. Further details regarding PYTECH's process can be found in a recent life cycle analysis [91].

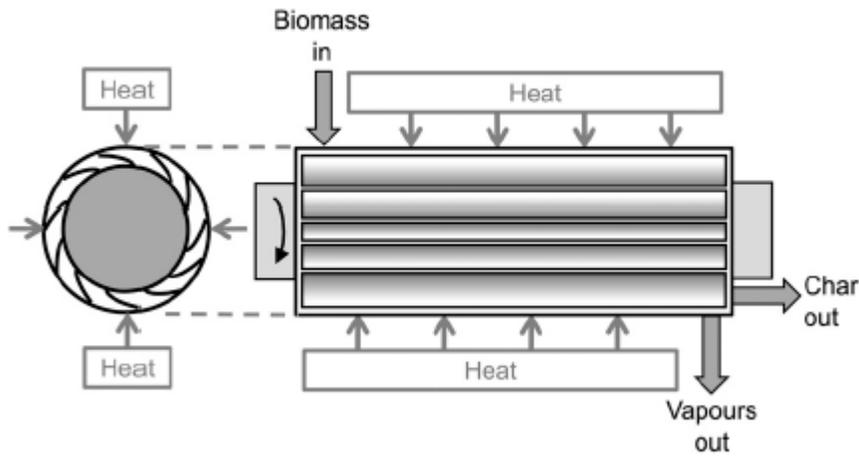


Figure 2.30. Diagram of Aston University Mark-2 ablative fast-pyrolysis reactor, reproduced from [1]

Mass and energy balance: Information from the only commercial company operating an ablative pyrolysis reactor (PYTECH) was used for the mass and energy balances [79, 91] due to the limited availability of information from other sources. However, it should be noted that reference [91] is a peer-reviewed article co-authored by PYTECH personnel. The process is integrated, where the fuel-gas is combusted to dry the feedstock entering the reactor and all the char plus 25 wt% of the product bio-oil is used to power the pyrolyzer and provide the on-site electricity.

The mass balance is approximately 65-75 wt% bio-oil, 5-10 wt% char and 15-25 wt% gas. The energy balance is approximately 64% in the bio-oil, 11% in the char and 13% in the fuel-gas, with about 12% lost during the process (based on energy in the biomass feedstock, $LHV_{a,r}$). Net thermal efficiency (process based) for the integrated process is roughly 60% ($LHV_{a,r}$) and the amount of bio-oil from 1 tonne of raw biomass input is 230 kg with a $LHV_{a,r}$ of ~ 15.5 MJ/kg (this is the only exportable product from an integrated process). The bio-oil is in a single phase and contains $\sim 25\%$ water. The moisture content of the starting biomass was not reported [79, 91].

The net and gross efficiencies for ablative reactors are within the range defined previously in Section 2.4.2.1.1. However, from the information available it seems that the ablative process is about 5-10% less efficient than fluidized-bed or rotating cone designs.

U3: Other reactor systems

Many other types of reactor have been studied at the laboratory and pilot scale and include fixed-bed, entrained flow, augur or screw, microwave, solar, vacuum and hydro-pyrolysis. However, they all suffer from drawbacks when scale-up is considered or have other complications. They are useful however, for fundamental studies and certain niche commercial applications. Further details on these reactor types can be found elsewhere [1, 5, 66, 81].

It is thought that at present the most efficient use of bio-oil from fast-pyrolysis is to generate combined heat and power (electricity) in a coupled system; i.e. where all the products from biomass pyrolysis are combusted in an interconnected reactor (boiler). This would mean that the bio-oil does not need to be recovered which greatly improves efficiency and technical drawbacks (i.e. the hot gases, vapors and aerosols and solids are sent directly to the boiler for combustion). Better heat integration and lower losses would also be expected. However, this means the only products are heat and electricity. VTT, Finland, are exploring this type of approach as well as other variations based on coupled systems [81, 84]. Also worth noting is work being carried out at the Energy Centre of the Netherland where coupled biomass pyrolysis-gasification systems for heat and power generation are being developed [90, 92].

Summary of fast-pyrolysis reactors

The mass and energy balances presented above for fast-pyrolysis reactors are 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 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 $LHV_{a,r}$ [5] and 70-80% when based on HHV_{dry} . Table 2.22 provides a break-down of these efficiencies

in terms of net, gross, fuel- and process-based values. The net efficiency is approximately 5% lower than the gross to account for addition 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 [93] and references therein, or even 95% [9]. However, these values are unlikely to be achieved at commercial-scale facilities. The efficiencies of processes used to upgrade bio-oil into transportation fuels are discussed in the following section, Section 2.4.2.1.4.

Table 2.22. Approximate efficiencies for bio-oil production from a generic fast-pyrolysis reactor, all values have a deviation of $\pm 10\%$ absolute.

	Basis	Symbol	LHV _{a,r} *	HHV _{dry}
Fuel	Net	Eff _{N-FB}	65	75
	Gross	Eff _{G-FB}	70	80
Process	Net	Eff _{N-PB}	60	70
	Gross	Eff _{G-PB}	65	75

*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 [1, 5, 94]. 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 [5, 94]. In this regard, despite common points of interest and shared challenges, research on coal and biomass pyrolysis has in the past been conducted with little reference to one another. The similarities and differences between the behaviors of these classes of samples would have seemed worth considering as instructive, as has been pointed out for other aspects of biomass research [95]. For further information regarding pyrolysis fundamentals related to coal and biomass see reference [83].

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 [5]. More emphasis should be

placed on understanding the fundamentals of pyrolysis chemistry and reducing pretreatment, recovery, stabilization and upgrading costs.

U4: Bio-oil recovery

The bio-oil exits a fast-pyrolysis reactor as vapors and aerosols which have to be quickly cooled and condensed (quenched) to avoid degradation of the bio-oil properties. The bio-oil also has to be free from char, ash and other particulate matter before it can be used. The recovery of bio-oil requires a number of different unit operations that are common to the three types of reactors described above. The only difference is in the size of the units. Ablative pyrolyzers have no bed material or carrier gas, hence fewer and much smaller units are required. The rotating cone designs can accommodate smaller unit scales than the fluidized-bed modules and downstream processing units are scaled accordingly [1, 5]. A break-down of the individual units required to recover bio-oil follows.

U4-A: Particulate matter (PM) removal

Char, ash and bed material (such as sand) are the main forms of PM that need to be removed from the bio-oil in fluidized-bed and rotating cone reactors. Due to the high viscosity of bio-oil, this is best achieved by cleaning the bio-oil before it is condensed. Cyclone filters are typically used for this purpose and are well understood and inexpensive; however, some fine PM remains as a contaminant in the bio-oil [1, 5]. Hot vapor filtration (similar to hot gas filtration in gasification) is another promising method that offers better fine PM removal. However, this method suffers from the sticky nature of the oil vapors and char, which block the filters and make de-caking difficult. Hot filtration of the liquid bio-oil is a common method of PM removal; however, this is less favorable as it requires additional energy for re-heating and pressurizing the bio-oil [1, 5]. Work is ongoing to find better ways of removing PM from the hot vapor.

U4-B: Quenching (condensation and cooling)

Condensation of the bio-oil from the vapor phase is typically achieved in two steps. First, the vapors are recovered by quenching in already recovered product bio-oil or an immiscible hydrocarbon solvent; followed by electrostatic precipitation of aerosols. Other combinations of methods are possible but quenching and ESP are widely considered the most effective at present

[1, 5]. The second step is mainly required for fluidized-bed reactors where there is a low concentration and partial pressure of vapors and aerosols in the carrier gas due to the relatively high flows required for fluidization [1, 5].

Rotating cone reactors use less carrier gas than FB reactors and can therefore use smaller quench units [1, 3, 85]. Ablative reactors do not use a carrier gas, therefore requiring the smallest gas-cleaning units [1, 91].

U4-C: Storage

Bio-oil as part of an industrial process would typically be stored 3 to 12 months prior to transportation or use. The acidity and instability of bio-oil, however, makes storage and transportation problematic, as does its immiscibility with conventional fuels [1, 5, 66, 74].

Instability: Bio-oil is typically reactive (unstable) at room temperature and in the presence of air (oxygen) polymerizes to form lower value products, a process known as ageing [1, 5]. Bio-oils must therefore be stabilized before storage or transportation. Current practice is to add alcohols (~10% by weight) to stabilize bio-oils before storage. This reduces ageing by a factor of at least twenty times [1, 5]. Methanol is preferable but ethanol is often more practical; however, cheaper alternatives are desirable [74]. Another approach is to make an emulsion of the bio-oil with diesel using surfactants; however, this method has yet to be proven commercially viable [5]. Further research is required to find more effective ways to stabilize bio-oils.

Acidity: Bio-oil is acidic (pH 2 to 3) due to the high oxygen content and therefore incompatible with common steel storage and transportation vessels used in the petroleum industry. Corrosion resistant materials have to be used which increases the cost of storage and transportation. No methods are currently available for modifying the acidity of bio-oils on a commercial-scale [1, 5]. Esterification processes are being studied and are discussed in Section 2.4.2.1.4.

Immiscibility: Bio-oil is immiscible with petroleum derived liquids, therefore requiring dedicated infrastructure for transportation, i.e. pipelines and tankers (road and ocean) [1, 5].

Once the bio-oil is recovered it has a number of potential applications / processing routes. Broadly speaking, there are two applications:

- i) upgrading: bio-oil used as an intermediate for the production of transportation fuels (biofuels) and chemicals;
- ii) direct use of bio-oil as a fuel (heat and electricity).

Each application has a variety of possible processing routes that could be used. Upgrading is discussed next in Section 2.4.2.1.4 and direct applications in Section 2.4.2.1.5.

2.4.2.1.4 Upgrading of bio-oil module (M_{up})

Bio-oils as intermediate: 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 (cf. Table 2.21) [1, 5, 74]. 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, 5]. A summary of the upgrading methods for fast-pyrolysis products is shown in Figure 2.31. Further descriptions of the main approaches follow.

Comprehensive reviews of upgrading methods for bio-oils including detailed technical and economic information have been reported [1, 5, 66, 81]. The main conclusions reported herein are a brief summary of information from those articles.

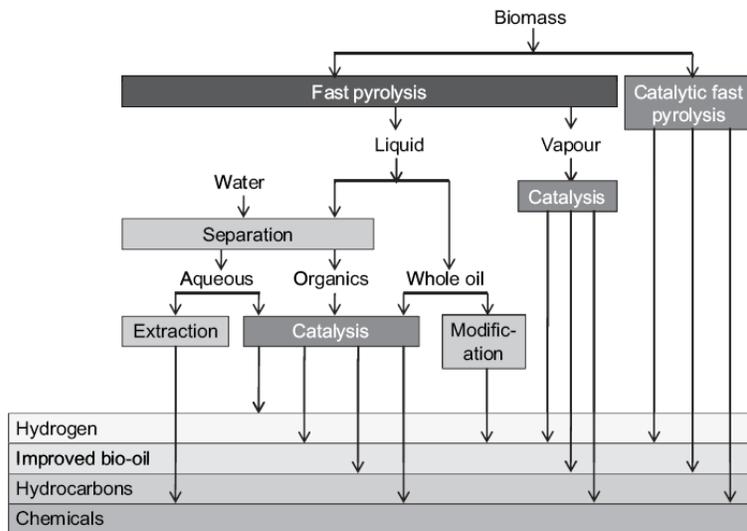


Figure 2.31. Overview of fast-pyrolysis upgrading methods, reproduced from [1]

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 [1]:

- 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

An overview of the methods for upgrading bio-oil to biofuels and chemicals is depicted in Figure 2.32. Given all the potential options and the lack of information from commercial companies, it is not possible to identify a ‘best route’ at present.

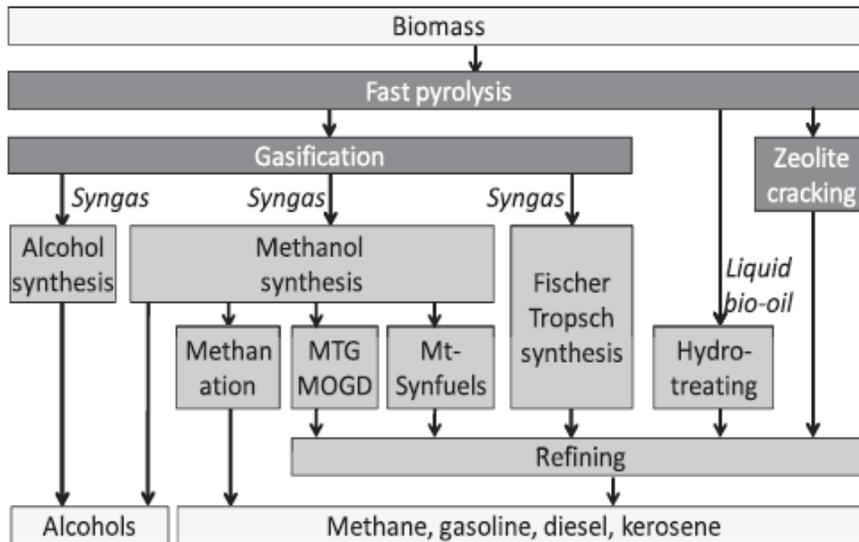


Figure 2.32. Upgrading of bio-oil to biofuels and chemicals, reproduced from [1]

1) Hydro-treatment

Hydro-treatment of bio-oil involves de-oxygenation through a catalytic process which results in a naphtha-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, 5, 66].

The expected typical yield of naphtha 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 [1]. 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 [1]. 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 [1].

The catalysts traditionally used for hydro-treatment are CoMo and NiMo on alumina or alumina-silicate supports [1]. 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, Groningen University 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, 5, 66]. The main concerns for hydro-treatment are coke and gas formation as well as catalyst deactivation and the high pressure and hydrogen requirements [1, 5].

As previously mentioned, UOP LLC is building a 1 t/d (dry-input) pilot scale unit at the Tesoro refinery in Hawaii. From available information [2, 80, 86, 88, 96], 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 proprietary. It has been reported by UOP at a recent conference [2, 86] 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% [2].

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-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 52% 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 [5] (on a HHV basis). In a separate review article, a Eff_{N-PB} of 33% was reported [1] (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 [5]. This operation can be integrated with the pyrolysis step or performed remotely on bio-oil or revaporized bio-oil. Figure 2.33 gives an overview of these process routes [1].

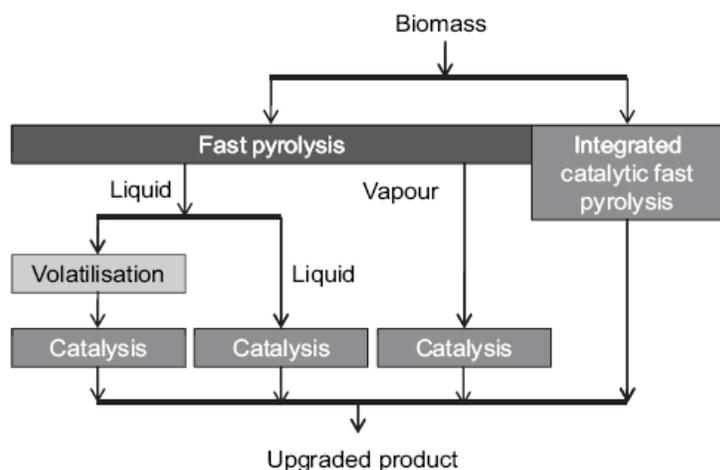


Figure 2.33. Methods of upgrading fast-pyrolysis products with Zeolite cracking, reproduced from [1]

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, 5, 66]. 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 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 [1, 97]. 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 [1]. However, it is unlikely that methods which involve impregnating biomass with a catalyst would be viable in a commercial 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 [1]. Several other groups and commercial companies are active [1, 5].

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, 5].

(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, 5]. 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 [1].

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, 5].

(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, and the others mentioned above, can be found elsewhere [5].

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 at present [1, 5]. 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 [1].

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, 5].

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 adopted 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 [1]. 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, 5, 97-100]. 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.

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 [1]. 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, 66]. 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 [1]. For example, phenol and poly-aromatic

hydrocarbons can be cracked using commercial nickel-based catalysts such as G91 from Süd Chemie [101].

Gasification with Fischer-Tropsch synthesis of liquid fuels and chemicals

This production concept includes de-centralized production of bio-oil and bio-oil/char slurries with transportation to a centralized gasification and synthesis plant [1, 5, 66]. The resulting syngas can then be synthesized into FT products or alcohols as shown in Figure 2.32. This route is reported to incur a small energy penalty because of the use of pyrolysis, the required transportation energy and the additional bio-oil gasification step [1]. However, this is expected to be offset by the economy of scale that can be achieved at a commercially sized gasification and biofuels synthesis plant (typically 1 GW_{th}) [1]. Due to limited biomass resources of small island states such as Hawaii, this scale remains an unlikely scenario. Still, the concept of very large gasification plants (>5 GW_{th}) close to large ports capable of handling vast amounts of biomass has been suggested. However, this approach is deemed infeasible in Hawaii.

Gasification of bio-oil is possible in pressurized entrained flow oxygen-blown units such as those developed by Texaco or Shell [1]. Advantages of this method are the ease of feeding a liquid under pressure compared to solid biomass and better gas quality. Synthesis of transportation fuels at 50,000 to 200,000 barrels/day (8-32 million liters) output is reported to be commercially realistic based on current natural gas-to-liquids (GTL) plants operating world-wide [1]. SASOL (South Africa) has recently built a 34,000 barrels/day GTL facility in Ras Laffan Industrial City, Qatar (Oryx GTL). The largest GTL process currently operating is Pearl GTL in Qatar. At full capacity it can convert 1.6 billion cubic feet of natural gas per day into 140,000 barrels of petroleum liquids. In addition, it can simultaneously convert 120,000 barrels of oil equivalent per day (730 terra joules) into natural gas liquids and ethane [56, 102]. Siemens has demonstrated a similar approach for bio-oils and bio-oil/char slurries [1].

Synthesis of hydrocarbon biofuels can include drop in replacements for diesel, gasoline, natural gas, liquefied petroleum gas (LPG) and jet-fuel. These products are completely compatible with petroleum fuels and fuel systems and can be refined conventionally. The approach of replacing petroleum derived fuels with drop-in bio-based replacements is widely considered the most acceptable to consumers in the short to medium term [1, 3, 5, 66]. However, as mentioned

earlier, the scale required for these processes makes them unlikely to be suitable for the requirements in Hawaii.

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 [6, 81, 85]. 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 [5]. 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 [1].

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) [2, 4].

A reoccurring conclusion from the review articles used as sources for this report was the need for further research into upgrading methods are necessary to reduce production costs and improve conversion efficiency [1, 5, 66, 76, 94].

2.4.2.1.5 Applications of bio-oil (M_{ap})

Bio-oil as fuel (end-product): Bio-oil can be substituted for petroleum fuels in certain combustion applications [1, 3, 5, 66]. For example, bio-oil can be used in existing power stations as a replacement for (or in combination with) low sulfur fuel oil (LSFO) after minor modifications to the burners and feed systems to account for the difference in heating value. This would typically be at small to large scale facilities (10-1,000 MW_e) [1, 66]. Some treatment of the bio-oil may be required before it can be combusted, such as filtering, use of additives, or blending with conventional fuels [1, 2, 5].

Bio-oil has been shown to be suitable for combustion in stationary diesel generators for combined heat and power (electricity) after minor modifications to the engine (up to 15 MWe has been reported to be currently feasible) [66]. Mixing of bio-oils with diesel is another possible route. However, this is costly due to need for surfactants and energy for emulsification [5]. Tests of mixed bio-oil and diesel in diesel generators have been shown to increase corrosion [5]. The longest reported tests are those undertaken by PYTECH who have been using their bio-oils in 315 kW CHP diesel generators since 2006; although it is unclear if continual operation has been achieved. It should be noted that additives are required to reduce corrosion and emissions and that the engine is also derated from the nameplate 450 kW [91].

Using bio-oil to power gas turbines is reported to result in greater wear of the blades and increased deposition of inorganics compared to conventional fuels. Therefore, turbine processes do not appear to be viable at present [1, 66]. It has also been reported that bio-oil from Dynamotive's process has been tested in turbine applications, but long terms tests proved unsuccessful [91]. These issues relate to residual ash in the bio-oil and can be (partly) overcome with better removal of particulate matter. Magellan Aerospace has gas turbines that can operate on 'conventional biofuels' such as standardized ASTM certified biodiesel, ethanol and possibly on bio-oil from fast-pyrolysis. However, due to the lack of commercial bio-oil production and the inconsistent quality of the bio-oil they received, only limited tests have been possible [82]. The economics are generally not attractive for electricity generation on a small scale (less than 15 MW_e) unless operated in a cogeneration configuration for heat and power [82].

Co-firing or co-processing of untreated biomass with coal is widely performed at commercial-scales, with about 5% of the thermal input supplied by the biomass. The primary benefit is the economies of scale available from large coal units. Processing biomass for feeding into coal fired boilers must be addressed [3]. Co-firing a boiler with bio-oil and coal has also been demonstrated at two power stations located in the USA (Manitowac and Red Arrow) with no adverse effects [1]. The proportion of bio-oil co-fired and the duration of the tests were not disclosed. Bio-oil has also been successfully co-fired with natural gas in the Netherlands; however, limited information is available [1]. UOP indicates that RTP green fuel (bio-oil) is suitable for direct combustion in boiler applications to generate heat and/or power and is suitable for co-firing with coal or other fossil fuels with appropriate fuel handling modifications [2]. Information on the

scale, duration and performance of the tests is proprietary. Figure 2.29 gives a summary of potential applications for fast-pyrolysis products from biomass.

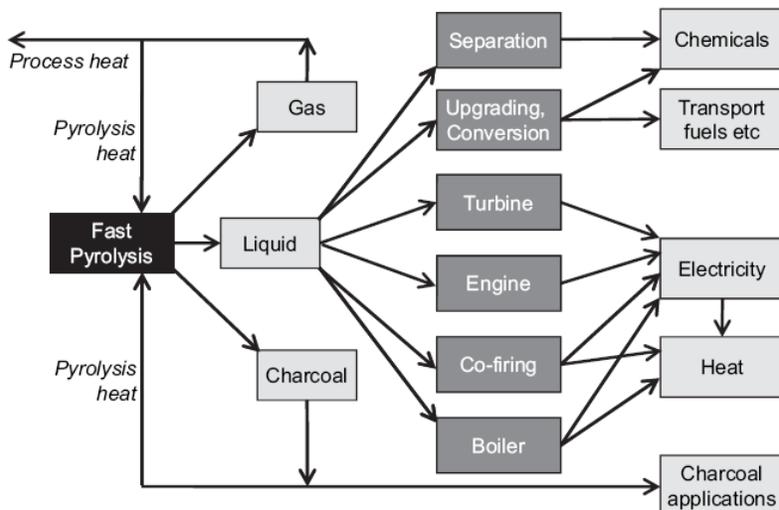


Figure 2.29. Potential applications for biomass fast-pyrolysis products, reproduced from [1]; char is referred to as 'charcoal' in this figure.

2.4.2.1.6 Pyrolysis based bio-refinery

When considering the use of biomass as a resource for fuels and energy in a move away from fossil fuels, it is important to remember that most chemicals are derived from petroleum. In a petroleum refinery, approximately 5% of the crude oil is used to produce chemicals other than fuels and the value of the chemicals is on the same level as the fuel and energy products [1]. Therefore the concept of a bio-refinery is attractive to offset the high cost of fuel and energy production from biomass [1, 3, 5, 66]. As biomass is more heterogeneous than petroleum, it is reported to be better suited for chemicals production (most chemicals contain hetero-atoms in their structure) [1].

A bio-refinery would produce transportation fuels, energy and chemicals. Figure 2.35 depicts one example of a pyrolysis based bio-refinery. However, the biorefinery shown in Figure 2.35 is unlikely to be suitable for Hawaii as it is integrated. A commercial facility in Hawaii is more likely to incorporate a reduced subset of these processes. Gasification of biomass for synthesis of biofuels and chemicals is another possibility. However, it has been reported that most of the

energy is lost during the process, and that electricity generation is probably a better option [1]. A similar conclusion was reached in a separate review article [5].

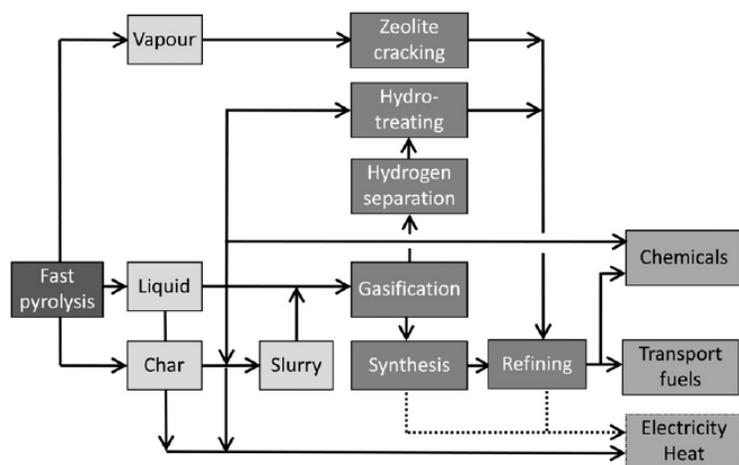


Figure 2.35. Fast-pyrolysis based bio-refinery, reproduced from [1]

When considering the production of chemicals from biomass it is important to note that biomass compositions are variable depending on plant type and geographic location, more so than petroleum [1, 95]. Therefore, it is possible that region specific processes will need to be developed / implemented. In addition, biomass has a generic empirical formula of approximately $(CH_{1.5}O_{0.7})_n$ whereas for petroleum it is $(CH_2)_n$ which means standard refinery practices can no longer be used and new formulations must be developed to manufacture chemical products.

It is important to consider the value of the different components of biomass and to match their utilization to the most efficient and cost effective processes to make a viable bio-refinery. For example, Dynamotive reports a bio-oil to transportation fuels upgrading process where meaningful quantities of methanol and acetic acid can also be recovered [4]. Elsewhere it has been suggested that high value chemicals can be produced from vegetable oils relatively easily and, it is therefore wasteful to simply burn them [1]. Likewise, little attention has been paid to the uses of char other than as a fuel. It is probable that chars will find high value applications in the production of absorbents, as a reductant for metallurgy or other advanced carbon materials and composites (carbon fibers, etc.) [64, 103-107] as well as a soil amendment (cf. Section

2.4.2.2.4) [67, 108-110]. Biomass ashes may also become a valuable source for catalysts or fertilizer production when heavy or precious metals as well as potassium or phosphorous are reclaimed [95, 110]. It is also important to consider waste streams from each process as well as environmental concerns and social impacts [95].

One example of an integrated bio-chemical and thermochemical bio-refinery is shown in Figure 2.36 [1]. Although this type of integrated facility is more cost effective when economies of scale and integration can be realized, it is unlikely to be suitable for Hawaii. A more likely scenario in Hawaii would be decoupled sub-sets of these processes feeding one centralized upgrading and refining facility as described in Section 3.

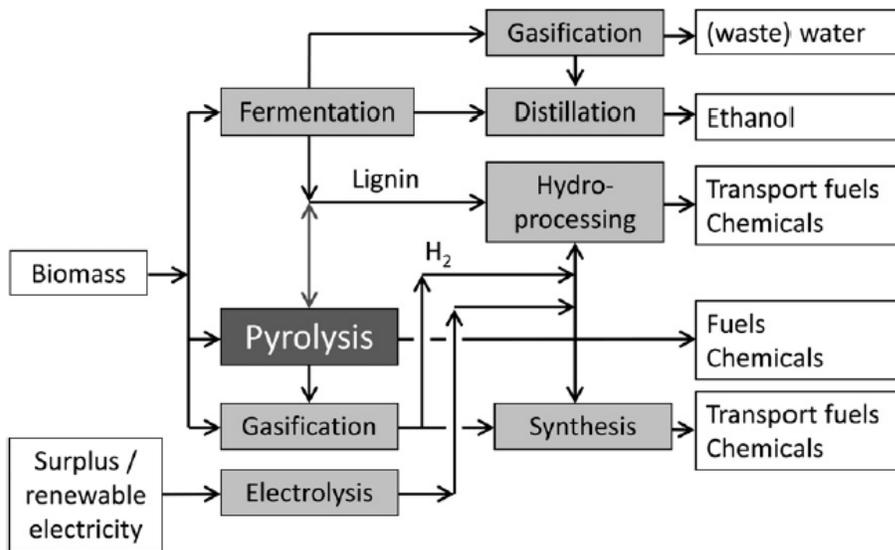


Figure 2.36. A bio-refinery concept based on integrated biological and thermal processing for transportation fuels and chemicals, reproduced from [1]

2.4.2.1.7 Economic evaluation (fast-pyrolysis for bio-oil)

In this section cost data for producing bio-oil is discussed. This is followed by cost estimates for upgrading bio-oil to 'drop-in' replacement transportation fuels, and finally for producing electricity from bio-oil.

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 $25 \text{ MW}_{\text{th(input)}}$ ($\sim 350 \text{ t/d}$ input of biomass with 50% M.C, $\text{LHV}_{\text{a,r}} 6.2 \text{ MJ/kg}$) pyrolysis unit which includes feedstock preparation, dryer, hammer mill, rotating cone pyrolysis reactor, gas cleaning and bio-oil recovery [3]. The capital investment costs were between \$5.6 and 14.4 million. Production costs, excluding the cost of feedstock, were given as \$94-188/t of bio-oil (Table 2.24), which is equivalent to \$7.5-15/GJ (published 2008) [3].

A summary of the techno-economic study from reference [3] is reproduced in Tables 2.23-24 and compares fast-pyrolysis for bio-oil production with torrefaction, torrefaction combined with pelletization (TOP) and conventional biomass pelletization. In this economic evaluation, a scale of $40 \text{ MW}_{\text{th(input)}}$ was used for normalizing the data (560 t/d input of biomass with 50% M.C, $\text{LHV}_{\text{a,r}} 6.2 \text{ MJ/kg}$). In the accompanying sensitivity analysis it was noted that the economies of scale have a considerable influence on the production costs. For torrefaction it was stated that after $40 \text{ MW}_{\text{th(input)}}$ the specific investment costs do not decrease any further, whereas production at smaller capacities increases costs significantly. For pyrolysis processes, capacities greater than $25 \text{ MW}_{\text{th(input)}}$ ($\sim 350 \text{ t/d}$ input of biomass with 50% M.C, $\text{LHV}_{\text{a,r}} 6.2 \text{ MJ/kg}$) do not benefit greatly from economies of scales (although they do continue to decrease) and are most competitive against torrefaction and pelletization at scales of less than $25 \text{ MW}_{\text{th(input)}}$ [3]. It should be noted that the net process-based efficiency stated in Table 2.23 for the torrefaction process is greater than 90% (as reported in reference [3]). However, in a more recent review article a value of 80% was assumed to be more realistic for a commercial-scale facility [72]. Refer to Section 2.4.1 for further details on torrefaction and other pretreatment technologies outlined in Table 2.23.

Table 2.23. Technical comparison of torrefaction, TOP, pyrolysis and pelletization processes, reproduced from [3]

	Unit	Torrefaction	TOP	Pyrolysis	Pelletization
Feedstock		Woodcutting chips	Green wood chips	Clean wood waste	Green wood chips
Moisture content (M.C.)	wt%	50	57	-	57
LHV (as-received)	MJ/kg	6.2	6.2	6.2	6.2
Product type		Torrefied biomass	Torrefied Pellets	Bio-oil	Pellets
Product M.C. (average)	wt%	3	1-5	20-30 (~22)	7-10
Product LHV _{a,r} (dry)	MJ/kg	19.9 (20.4)	19.9-21.6 (20.4-22.7)	17	15.8 (17.7)
Bulk mass density	kg/m ³	230	750-850	1200	500-650
Bulk energy density	GJ/m ³	4.6	14.9-18.4	20-30	7.8-10.5
Thermal efficiency ^a	LHV _{a,r}	96%	92-97%	66%	92.2%
Net efficiency ^b	LHV _{a,r}	92% ^c	90-95% ^d	64% ^e	84% ^f

^a Net fuel-based efficiency indicates the efficiency where utility use is not included (energy of product / energy of feedstock), i.e. as defined in Section 2.4.2.1.1.

^b Net process-based efficiency includes primary (utility) energy use to produce power necessary for components in the plant, i.e. as defined in Section 2.4.2.1.1.

^c The electrical input to the system is given as 2.61 MW_e for 517,000 t/y feedstock input.

^d Utility fuel consumption is measured as 4.7 MW_{th} and electricity consumption as 1.01 MW_e for 170,000 t/y feedstock input.

^e Pyrolysis electricity consumption is accepted as 0.015 MW_e/MW_{th}, electricity is assumed to be generated with 40% efficiency.

^f The utility fuel consumption is measured as 11.3 MW_{th} and electric consumption as 1.84 MW_e for 170,000 t/y input. When sawdust is used, the net efficiency is around 88%.

Table 2.24. Economic comparison of torrefaction, TOP, pyrolysis and pelletization processes (feedstock cost is not accounted for), adapted to \$ from [3]

	Unit	Torrefaction	TOP	Pyrolysis	Pelletization
Normalized capacity	MW _{th(input)}	40	40	40	40
Capital investment	M\$	8.1	9.8	7.8-19.9	7.8
Specific investment	M\$ / MW _{th(input)}	0.21	0.24	0.20-0.50	0.19
O&M ^b	%	5	5	4	5
Energy consumption	kWh/t _(input)	92	102	75	129
Production cost ^a	\$/t	72.5	62.5	94-188	67.5
Production cost ^a	\$/GJ	4.0	3.1	7.5-15.0	4.3

^a Assumptions for TOP and torrefaction, 8,000 h load factor, 10-year depreciation; for pyrolysis 7,500 h load factor, 15-year depreciation; and for pelletization 7,884 h/y load factor. Feedstock cost is excluded.

^b O&M, operation and maintenance.

The data provided in Tables 2.23-24 assume a biorefinery with 40 MW thermal input. This corresponds to 560 t/d of freshly harvested biomass (50% moisture content and LHV_{a,r} of 6.2 MJ/kg) or ~200,000 t/y.

In a more recent study (published 2011), the cost of production of bio-oil by fast-pyrolysis was estimated [1]. The assessment includes the complete installation costs, from dry-feed preparation through product bio-oil storage (ready for transport). Figure 2.37 shows the estimated cost (\$/t) for bio-oil production at different throughput, starting at 1,000 t/y biomass dry-feed and considering four different biomass feed costs (0, 40, 60 and 100 \$/t). 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 [1]. Note that the type of pyrolysis unit was not identified.

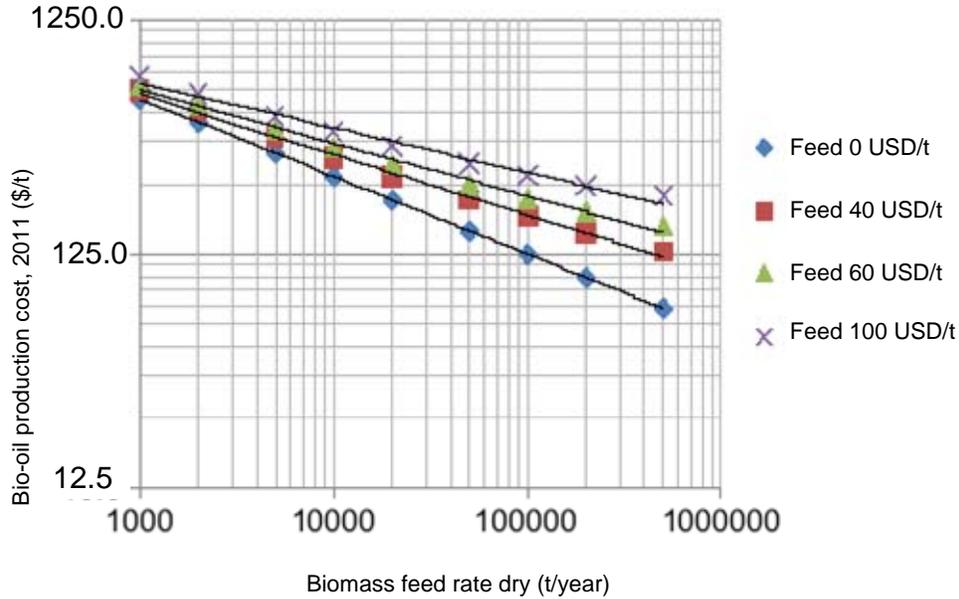


Figure 2.37. Bio-oil production costs, adapted from [1]

Based on the economic assessment presented in Figure 2.37 it can be estimated that the cost of bio-oil production is roughly equivalent to imported low sulfur fuel oil (LSFO):

Bio-oil \cong \$750/t in the worst case (biomass feed rate 1,000 t/y at \$100/t)

LSFO \cong \$700/t (2012 price in Hawaii)*

*Price calculated from the ‘Hawaiian Electric Company 2012 fuel forecast’, using the reference value for LSFO in nominal dollars, the cost is forecast to rise to \$850/t by 2015.

However, bio-oil contains roughly half the heating value of LSFO ($LHV_{a,r} \sim 17$ MJ/kg and 40 MJ/kg, respectively). Therefore, for bio-oil to be cost competitive against LSFO on an equal energy basis, its cost per tonne has to be roughly half that of LSFO (i.e. \sim \$300/t). From the data in Figure 2.37, bio-oil would have to be produced from a dry-biomass feed rate of approximately 10,000 t/y (27 t/d) to realize production costs of \sim \$250 to \$380/t, depending on feedstock cost, Figure 2.37. 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 listed as follows:

Circulating FB = 400 t/d (140,000 t/y or 116,000 t/y_{80%*}) – Envergent

Bubbling FB = 200 t/d (70,000 t/y or 58,000 t/y_{80%*}) –RTI/Dynamotive

Rotating Cone = 120 t/d (44,000 t/y or 35,000 t/y_{80%*}) – BTG

*t/y_{80%} refers to an operating availability of 80% of the year, 292 days per year;
t/y is 365 days.

Dynamotive reports [4] a bio-oil production cost of \$400/t based on a 400 t/d (dry-input) plant (i.e. two 200 t/d units) and a feedstock cost of \$30/t_(dry). More expensive feedstock of \$130/t_(dry) will result in a bio-oil cost of \$715/t. No details regarding capital cost or the basis of the cost estimates were provided [4].

From the data reproduced in Table 2.24, the estimated cost of bio-oil production is \$94 to 188/t at a scale of 40 MW_{th} (560 t/d biomass input with 50% moisture and LHV_{a,r} of 6.2 MJ/kg) [3]. This cost is higher than the other biomass pretreatment processes analyzed in the cited study [3]. However, it is cheaper than the other price estimates for bio-oil given above, or for LSFO imported to Hawaii (on an energy equivalent basis). However, the feedstock costs are *not* accounted for in this cost estimate.

A comprehensive review article from 2006 estimated the minimum selling price for fast-pyrolysis bio-oil as \$145/t and with continued R&D it could potentially reach \$110/t [5]. The minimum selling price accounts for capital as well as fixed and variable operation costs and a feedstock cost of \$60/t_(dry). The capital investment was reported to be \$50 million with the potential of being reduced to \$26 million with continued R&D. This is for a scale of 1,000 t/d dry biomass input.

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 hydro-treatment [5, 6, 81, 85]. A thorough report of a design case for this process was published in 2009 by Pacific Northwest National Laboratory [6]. It was concluded that the capital cost for a plant design capacity of 2,000 t/d dry biomass, 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. Co-locating the plant with an existing refinery could reduce the capital investment to \$188 million and the minimum fuel selling price to \$1.74/gal. It should be noted that the scale considered in the design case [6] is 2,000 t/d input dry biomass. At a smaller scale (500 t/d input dry biomass), the minimum fuels selling prices increases to \$2.68/gal. Capital cost for a 500 t/d unit was not given [6].

A scale of 500 t/d dry biomass input is large for a single fast-pyrolysis facility in Hawaii; however, it is within the range that is feasible (cf. Section 3). The cost estimate for gasoline and diesel production at this scale is ~ \$3/gal (2007 price [6]), compared to current pump prices for gasoline and diesel in Honolulu (\$4.41/gal and \$4.85/gal, respectively, that each include at least \$0.335 in taxes [111, 112]). 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 “nth” state of development [6]. 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 hydro-treatment was estimated to be \$2.2/gal with the potential of being reduced to \$1.8/gal with continued R&D [5]. The minimum selling price accounts for capital as well as fixed and variable operation costs and a feedstock cost of \$60/t_(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 t/d dry biomass input.

From the most recent press release available from Dynamotive’s website (Sept. 2012 [4]) the current cost of producing replacement gasoline and diesel using their process is \$4.55/gal total fuel, projected to reach \$2.32/gal by 2017. Capital costs were not given.

The cost of producing transportation fuels from bio-oil with upgrading achieved via oxygen blown entrained flow gasification and Fischer-Tropsch (EFG-FT) synthesis has been evaluated (FT conversion efficiency was assumed to be 71%) [3]. The cost was estimated to be \$12.3/GJ_{HHV} when accounting for the entire processing and delivery chain, from harvest, shipping through to production of transportation fuels [3]. Based on one liter of diesel containing 38 MJ of energy (HHV), the cost of production is approximately \$1.8/gal of diesel equivalent fuel. This assessment was published in 2008 and the cost estimate includes shipping the bio-oil from South American to Western Europe (~7,000 miles) [3].

A break down 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 2.25.

Table 2.25. Cost of chains delivering FT-liquids from different pretreatment processes (\$/GJ_{HHV} liquid fuel delivered), adapted from [3]

Step in the chain	TOP	Pelletization	Pyrolysis (rotating cone)
Product	FT Liquids		
Units	\$/GJ _{HHV} liquids (biofuel)		
Conversion*	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) ^{&}	1.3	1.4	1.8

*conversion includes pretreatment and final conversion

[&]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}.

Cost estimates for producing electricity from bio-oil

Costs for the production of FT-liquids and electricity from bio-oil (rotating cone), TOP pellets and regular pellets after delivery to an import harbor are listed in Table 2.26 [3]. The cost estimates are for the entire processing chain from harvest, transportation by truck and ship to a final conversion facility. It should be noted that the transportation distance by ship in this analysis was approximately 7,000 miles (from South American to Western Europe) [3]. In addition, bio-oil was only considered to be suitable for co-firing to produce electricity with an efficiency of 40%. TOP and pellets were also considered suitable for firing in biomass integrated gasification combined cycle (BIGCC) and fluidized-bed combustion (FB-comb.) processes with assumed efficiencies for electricity production of 56% and 35%, respectively [3].

Table 2.26. Cost of FT-liquids and power based on delivered cost of intermediate fuel products and a \$12.50/t cost of biomass, adapted from [3]

	Intermediate delivered to import harbor	FT-liquid fuel	Power (BIGCC)	Power (FB-comb.)	Power (co-firing)
Unit	\$/GJ _{HHV}	\$/GJ _{HHV} (\$/gal)	US cents /kWh _e	US cents /kWh _e	US cents /kWh _e
TOP	4.1	9.3 (1.3)	5.8	9.6	5.8
Pellet	4.9	9.9 (1.4)	6.9	10.3	6.0
Bio-oil	5.9	12.3 (1.8)	-	-	7.4

Net efficiencies of chains for delivering electricity or FT-liquids

As described above, chains for supplying electricity or FT liquids from pretreated biomass (TOP, pellets and bio-oil) were evaluated in reference [3] in terms of economic and technical features (as shown in Tables 2.24-26). The related net process-based efficiencies were also assessed. It was reported that the highest efficiencies are 52% for TOP with BIGCC for electricity production and 61% for FT-liquids from TOP. For bio-oil, electricity was assumed to be produced from co-firing which results in a net efficiency of 32%, whereas FT-liquids could be produced at 44%. These values were based on conversion efficiencies (based on LHV_{a,r}) for electricity generation of 56% for BIGCC and 40% for co-firing, and for FT-liquids via EFG-FT at 71% [3].

Summary of the techno-economic assessment of biomass pretreatment processes

The cost of producing bio-oil from literature sources ranges from approximately

- \$100-150/t in 2006 including all costs [5];
- \$100-200/t in 2008 excluding capital investment costs and feedstock cost [3];
- \$250-750/t in 2011 including capital costs [1];
- \$400-715/t in 2012 including feedstock cost from a commercial company's website (no details were provided regarding the basis for the values) [4].

Prices vary depending on scale and/or feedstock cost, but generally compare favorably with costs of LSFO imported to Hawaii on an equivalent energy basis.

When 'drop in' transportation fuels are considered as the final product from bio-oil, cost estimates range from:

- ~\$2/gal in 2008 using EFG-FT (feedstock and capital costs for EFG-FT plant were not accounted for) [3];
- ~\$2/gal in 2006 using hydro-treatment (including all costs) [5];
- ~\$3/gal in 2009 using hydro-treatment (not accounting for capital costs) [6],
- ~\$4.6/gal in 2012 using hydro-reforming from a company website (no information regarding capital cost) [4].

Prices for gasoline and diesel in Honolulu (June 2012) are \$4.41/gal and \$4.85/gal, respectively, inclusive of tax, ~\$0.335/gal [111, 112].

Table 2.26 provides a summary of the findings of supply chain analysis for producing FT-liquids (transportation fuels) and power (electricity) from pretreated biomass [3]. Table 2.27 summarizes the techno-economic assessment for producing pretreated biomass, i.e. bio-oil, torrefied biomass, torrefied and pelletized biomass and biomass pellets. The main factors influencing production costs were plantation yield, interest rate (on capital investment), load factor of the conversion facility and plantation distance from the harbor [3]. The base cases used in the cited study were:

- plantation yield of 22.4 t_(dry)/ha yr,

- interest rate of 10%,
- harvest operation window of 8 month (OW)
- distance to harbor of 60 miles

It was found that increasing the OW to 12 months decreased production costs by up to 25%, increasing the interest to 20% increases costs by 33% [3]. Increasing the harvest yield to 150% of the base case decreases cost by up to 11% [3]. Increasing the trucking distance to 120 miles increases costs by up to 20% [3]. When these variables are considered for the conditions in Hawaii, pretreated production costs could be reduced by up to 40%, as the trucking distance is unlikely to exceed 60 miles and an OW of greater than 8 months is possible. This is without considering the much reduced inter-island shipping distances in Hawaii compared to the 7000 mile ocean shipping requirement used in reference [3].

Table 2.27. Techno economic comparison of torrefaction, TOP, pelletization and pyrolysis (bio-oil), adapted from [3]

	Unit	Torrefaction	TOP	Pyrolysis	Pelletization
Net efficiency*		92%	90-95%	64%	84%
Energy content (LHV _{drv})	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	\$/t	72.5	62.5	94-188	67.5

*Net efficiency, process-based as defined in Table 2.23.

The assessment reported in reference [3] concluded that the TOP process is optimal, and that pyrolysis derived bio-oil cannot compete on energy efficiency terms with TOP or pelletization (also when comparing the whole chain from biomass production to final conversion). However, it should be noted that torrefaction is yet to be proven at a commercial-scale and this assessment was published in 2008. In addition, the net process-based efficiency for torrefaction used in that study (92%, Table 2.27 [3]) is higher than those reported in a more recent review article (80% [72]). Moreover, the net process-based efficiency assumed for fast-pyrolysis in reference [3] to derive the cost estimates was 64%, whereas values of ~70% could be achievable using current

state-of-the-art, commercially-available reactors with full system integration and optimization. Finally, the electricity and FT-liquids generation methods need to be considered in light of existing infrastructure, as their costs were not accounted for.

It is apparent that pelletization should not be dismissed as a short term option until torrefaction is developed and validated, and/or bio-oil production costs can be shown to be reduced. It is also important to note that wood pellets can only be co-fired with coal at approximately 10-15% by weight (about 5% in terms of energy content), whereas bio-oils are likely to be capable of replacing a greater quantity of coal (in terms of energy displacement) and can be more easily co-fired with LSFO than wood pellets.

Average electricity price in Hawaii, residential use in nominal value, was \$0.24/kWh in 2009, \$0.33/kWh in 2008 and \$0.25/kWh in 2007 [113]. The cost of the fuel element in electricity production in Hawaii in 2011 was \$0.23/kWh (based on LSFO) with a total cost to the consumer of \$0.37/kWh [113]. Considering these prices are high compared to US mainland or EU averages it can be seen that all of the biomass process routes outlined in Table 2.26 appear competitive. However, it is important to state that in the assessment cited [3] the power plants were assumed to already exist which is not the case in Hawaii, except for the possibility of co-firing with coal or LSFO.

2.4.2.1.8 Summary and conclusions for fast-pyrolysis

Based on the various technological and economic studies described in Section 2.4.2.1.7 it can be seen that the pretreatment of biomass before utilization as a fuel appears beneficial. It is not straight forward, however to compare the production costs of bio-oils from different sources as the assumptions and/or basis 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. Refer to Section 2.4.2.1.7 for these details.

Pre-treated biomass in any of the forms mentioned in Table 2.26 seems to be cost competitive against LSFO for electricity production in Hawaii. Likewise, production cost estimates for bio-oils suggest they can be produced at a price comparable to LSFO imports [1, 4, 5].

Based on the assessments in references [5] and [6], transportation fuels produced from bio-oil upgraded by hydro-treatment also appears to be competitive against gasoline and diesel prices in Hawaii (roughly half the cost, ~\$2-3/gal). 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/gal diesel fuel equivalent (cf. Table 2.26, [3]). This is roughly half the price of diesel pump price in Hawaii as of June 2012 (\$4.4/gal [111]). The cost of producing ‘drop-in’ gasoline and diesel from biomass via fast-pyrolysis bio-oil, as reported by Dynamotive [4], is \$4.55/gal total fuel (diesel equivalent). This is significantly higher than those in the peer-reviewed literature and slightly higher than the pump price in Hawaii.

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 tonne 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 tonne of biomass will produce approximately 340 L (90 gallons, 290 kg), based on current estimates [2, 4, 86]. A summary of the yields of bio-oil and transportation fuels that could be produced per kilogram of dry biomass via fast-pyrolysis and hydro-treatment is presented in Table 2.28 along with their physical properties and costs, based on conservative estimates. The assumptions used to derive the values are provided in the foot-note to the table.

Table 2.28. 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

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*	%	~65	-
Energy density	MJ/gallon	71	137
Energy density	GJ/m ³	18.7	36.1
Cost	\$/t	700	1550
Cost	\$/GJ	44.9	36.5
Cost	\$/gallon	3.2	5.0

*Energy Conversion is for LHV_{a,r} values on a net fuel-basis (cf. Table 2.22).

Assumptions used:

Mass conversions as stated in the table. Specific density from [76], 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 reference [3] 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 [74]. Costs were estimated by assuming bio-oil has a production cost of \$700/t and transportation fuels \$5.0/gal. Biomass feedstock assumed to have a HHV_{dry} of 19.5 MJ/kg (LHV_{a,r} 16.8 MJ/kg when the moisture content is 6 wt% and the hydrogen content is 6 wt%). All the other properties were derived using these values.

2.4.2.2 Pyrolysis for Char Production

Thermochemical processes such as conventional (slow) pyrolysis - carbonization, fast (rapid/flash) pyrolysis and gasification produce char as a residue. Currently, charcoal is produced commercially from biomass using conventional pyrolysis processes, which are often referred to as carbonization. Accordingly, carbonization is often the term used to describe a biomass pyrolysis processes when the aim is to maximize the char yield. In general, chars derived from biomass have many advantages over other industrial heating agents (i.e. biomass and petroleum liquids or residues) such as low sulfur content, high fixed-carbon to ash ratio, relatively few inorganic impurities, specific pore structure with large surface area and little smoke discharge [66].

Traditionally, chars have been used as reductants for metallurgical processes (silicon and ferrous metals) [64, 105, 114], as well as feedstocks for producing advanced carbon materials [103, 104] such as sorbents (activated carbons), carbon molecular sieves, carbon fibers, co-polymers, etc. More recently, there is interest in using char for soil amendment to improve soil quality and to sequester carbon from the atmosphere [67, 108-110, 115], as will be discussed in Section 2.4.2.2.4.

2.4.2.2.1 Terminology and Definitions

Final constituents of pyrolysis can be categorized into gaseous, liquid (tar or bio-oil) and solid (bio-char, biocarbon, charcoal or char) products under standard temperature and pressure, whereby the solid fraction includes extractable compounds of large molecular weights [116]. However, no internationally recognized “standard method” for bio-oil and char recovery exists therefore bio-oil and char composition will vary not only with reactor type, feedstock and pyrolysis conditions but also with recovery conditions. Moreover, analytical characterization of these materials is not a trivial matter [67, 83, 117]. Consequently, chars and tars are ill-defined materials due to the inherent difficulties involved in recovering these materials in a consistent and reproducible manner, as well as the problems associated with their characterization using existing analytical chemistry methods [83, 90, 117].

In an effort to decrease the variety of terminology used in the literature for the solid residue of pyrolysis, this report will use the term ‘char’ when referring to the solid product from thermochemical treatment of biomass. When the char is specifically produced for use as a fuel, it will be referred to as ‘charcoal’. When the char is used for soil amendment it will be referred to as ‘bio-char’. It is important to note these terms are not related to any widely recognized definitions regarding the chemical or physical properties of the materials or their suitability to use as fuel, soil amendment or in other applications [67].

Definitions:

The ‘char yield’ has been defined as [69]

$$y_{\text{char}} = m_{\text{char}}/m_{\text{bio}}, \quad (2.10)$$

where m_{char} is the dry mass of product char and m_{bio} is the dry mass of the feedstock.

It is important to note that this definition (y_{char}) of the carbonization efficiency is intrinsically vague because the chemical composition of char is not defined [69]. A more useful measure of the carbonization efficiency has been defined as the fixed-carbon yield y_{fC} [69]

$$y_{\text{fC}} = y_{\text{char}} \times (\% \text{ fC}/(100 - \% \text{ feed ash})) \quad (2.11)$$

where % fC is the percentage of fixed-carbon content of the char and % feed ash is the percentage of ash content of the feedstock.

This yield (y_{fC}) represents the efficiency realized by the pyrolytic conversion of ash-free organic matter in the feedstock into a relatively pure, ash-free carbon [69]. It is useful to compare y_{fC} to the theoretical fixed-carbon yield at thermochemical equilibrium based on the compositions of the feedstock and reaction conditions (as explained elsewhere [69]). The theoretical thermochemical limit (TC_{eq}) can be considered as the maximum possible yield of fixed-carbon for a pyrolytic process and is referred to as the ‘ TC_{eq} limit’ [69].

When referring to the energy efficiency of pyrolysis for char processes, the following definition is used [69]

$$\eta_{\text{char}} = y_{\text{char}} \times (\text{HHV}_{\text{char}} / \text{HHV}_{\text{bio}}) \quad (2.12)$$

where η_{char} is the energy conversion efficiency, HHV_{char} is the HHV of the char and HHV_{bio} is the HHV of the dry feedstock. This definition is equivalent as the net fuel-based thermal efficiency ($\text{Eff}_{\text{N-FB}}$) defined previously in Section 2.4.2.1.1, i.e., $\text{Eff}_{\text{N-FB}} = \text{energy in product} / \text{energy in biomass}$.

2.4.2.2.2 Background of Conventional Pyrolysis, Yields & Efficiencies

Despite the long history of commercial charcoal production, current processes often use conventional pyrolysis methods which are remarkably slow and inefficient [69]. A typical yield of charcoal produced from hardwood in a Missouri kiln operated on a 7-12 day cycle is about 25 wt% [69]. This charcoal has a fixed-carbon content of ~80 wt% resulting in a fixed-carbon yield of ~20% [69]. Less efficient processes are widely employed in less developed countries and contribute to deforestation [69]. Uncontained atmospheric emissions from inefficient charcoal fuel production processes make it one of the most greenhouse-gas-intensive energy processes employed by man [69, 118].

Development of conventional pyrolysis

Concerns about the low efficiency of conventional pyrolysis for charcoal production led to one of the earliest publications (1851) in industrial chemistry research in France [64, 119]. It was noticed that higher yields of charcoal could be produced when conventional pyrolysis was performed at elevated pressure [64, 119]. These observations were confirmed by work in 1914-1915, another sixty years passed before interest in this phenomenon was reignited [64]. The most recent review of current and ongoing research in this area was published in 2012 [67], where the phenomena is explained as being due to the increased contact of tarry vapors with the char inside the reactor at high pressure, thereby favoring recombination reactions that increase the yield of char and fixed-carbon [64, 67, 69]. For a more in-depth analysis of the influence of reactor configuration and reaction conditions refer to references [5, 64, 83, 120].

The Flash Carbonization Process

Dr. Michael J Antal of the University of Hawaii has been a leading proponent of using elevated pressure for charcoal production since the 1970's and invented and patented the 'Flash Carbonization'TM process [26, 64, 69]. Flash Carbonization is a type of flash pyrolysis, which is performed at elevated pressure (100 psi or 7 bar), temperatures between 500-800°C and high heating rates ($> 1,000^{\circ}\text{C/s}$) to maximize the char yield [121]. Flash pyrolysis methods are optimized for liquids production (tar/oil) and are defined as having short solids residence times (<0.5 s), heating rates greater than $1,000^{\circ}\text{C/s}$ and temperatures between 700-1,000°C (cf. Table 2.18) [66]. When considering Flash Carbonization however, it is not meaningful to define the process in terms of gas and solids residence times due to the mode of operation, the through-put and fixed-carbon yield are more useful metrics [121].

Flash Carbonization, as performed in the reactor located at the University of Hawaii, can be described as follows [69]: the biomass feedstock is placed inside the reactor. Air is used to pressurize the vessel (145-290 psi, 10-20 bar), and a flash fire is ignited at the bottom of the bed. After a few minutes, air is supplied from the top of the reactor and the flash fire proceeds up the packed bed converting the biomass into char. The peak temperature reached during this process is typically 500-800°C [69]. The pilot scale reactor located at UH is currently operating at 50 kg/batch and 500 kg/batch after installation of a catalytic afterburner is complete. The reaction time is roughly 30 minutes, independent of scale [121].

The process can utilize feedstock with minimal size reduction, which reduces the energy and capital costs for chipping and milling (as required in other pyrolysis processes). In addition, using larger particles of biomass is beneficial as it has long been known that a lower char yield is obtained when using smaller particle sizes of biomass [75]. Air-dried (10-40 wt% moisture content) biomass can be used directly in the Flash Carbonization reactor without significantly reducing the fixed-carbon yield or energy conversion efficiency compared to oven dried feedstocks. However, the reaction time is significantly shorter for oven dried feedstocks [69]. For publically available information on the Flash Carbonization process refer to reference [26]. Literature articles related to different aspects of the process, as well as properties and uses of the chars produced, can be found in references [69, 105-107, 110, 120].

Flash Carbonization, feedstocks and yields

A number of feedstocks, that are available in the State of Hawaii, have been evaluated using the 50 kg/batch pilot scale reactor located at the University of Hawaii [64, 69]. These include *Leucaena*, corn cobs and macadamia nut shells (energy crop and agricultural crop residues). The approximate values for char yield, fixed-carbon yield, energy conversion efficiency, heating value, and fixed-carbon content for these feedstocks are presented in Table 2.29. The char produced from *Leucaena* has a fixed-carbon yield of 30% which is 95% of the TC_{eq} limit and retained ~60% of the energy of the dry wood feed (HHV basis). By changing the conditions inside the reactor (air-flow, peak temperature), metallurgical-grade char (coke) was produced. However, this resulted in a lower fixed-carbon yield to 80% of the TC_{eq} limit [69].

Table 2.29. Approximate value of char yields, fixed-carbon yields, energy conversion efficiency, heating value, and fixed-carbon content of Leucaena, corn cobs and macadamia nut shells, where the peak temperature was ~600°C; adapted from reference [69]

Sample	Char yield	Fixed-carbon yield	Energy conversion efficiency	Higher heating value - dry	Fixed-carbon content
Symbol	$y_{char}, \%$	$y_{fC}, \%$	$\eta_{char}, \%$	HHV _{dry} , MJ/kg	fC, wt%
<i>Leucaena</i>	40	30	60	33	80-90
Corn cobs	33	28	60	31	80-86
Macadamia nut shells	35	31	55	33	~90

Fixed-carbon yields of 28 and 31% were achieved for corn cobs and macadamia nut shells, respectively, which is equal to 100 and 90% of their respective theoretical TC_{eq} limits [69]. This compares favorably to conventional pyrolysis, which yields about 70% of the TC_{eq} limit. [64, 67, 69]. Other energy crops available in Hawaii, such as *Eucalyptus* and banagrass, have also been studied [105].

The main gaseous species emitted during Flash Carbonization (and conventional pyrolysis in general) include nitrogen, oxygen, methane, carbon monoxide, carbon dioxide, hydrogen and steam. The combustible gases from the Flash Carbonization of air dried *Leucaena* contained ~16.5% of the energy of the feed or ~3 MJ/kg *Leucaena* [69]. Additional energy may be

recovered as the process yields ~0.5 kg of steam per kg of air-dried *Leucaena* at a pressure of 145 psi (10 bar) [69].

The Flash Carbonization process has not yet been proven at commercial scales and although a number of techno-economic studies have been undertaken for potential licensees of the technology [121].

2.4.2.2.3 Summary for Pyrolysis for Char Production

Although conventional pyrolysis is the most common processes currently used to produce char from biomass, other technologies may provide higher char yields [67]. Char yields using conventional pyrolysis at laboratory scale range between 22-40 wt% (typically <35 wt%) depending on the feedstock and experimental conditions, whereas yields between 33-51 wt% have been achieved (typically 35-45 wt%) with Flash Carbonization [64, 67, 69]. This translates to higher char and fixed-carbon yields and a greater energy conversion efficiency than conventional pyrolysis, cf. Table 2.30 [67].

Other pyrolysis techniques such as fast-pyrolysis and catalytic fast-pyrolysis systems exist (as discussed in Section 2.4.2.1), which are primarily used to produce bio-oil also produce char. However, the char is typically combusted on site to provide heat to the pyrolyzer. In some instances the char can be recovered in useful quantities, as in Dynamotive's bubbling fluidized-bed process [4], referred to Section 2.4.2.1.3 for details. A thorough review of current technologies for carbonization of biomass has recently been published (2012), and the reader is referred to this article for further details [4].

A comparison of typical char yields from different thermochemical processes is provided in Table 2.30. It should be noted that although gasification is included in this list, the char is rarely recovered for export and is more often consumed on site for power generation. For further details on fast-pyrolysis and gasification, refer to Sections 2.4.2.1 and 2.4.3, respectively.

Table 2.30. Comparison of typical biomass char yields and properties obtained from different thermochemical processes [3, 5, 66, 67, 69, 76]

Process	Char yield	Fixed-carbon yield	Energy conversion efficiency	Higher heating value - dry	Fixed-carbon content
Symbol	y_{char}	y_{fC}	η_{char}	HHV _{dry}	fC
Units	%	%	%	MJ/kg	wt%
Conventional pyrolysis	25-35	~20	~40	~30	~80
Flash Carbonization	35-40	~30	55-60	30-33	80-90
Fast-pyrolysis	10-25	5-20	<30*	28-33	75-90
Gasification	0-10	0-10	<17*	31-35	95-100

*estimated by assuming the starting biomass has a HHV_{dry} of 19.5 MJ/kg, and only the energy in the char was accounted for (i.e. co-products were not considered)

2.4.2.2.4 Bio-char: Biomass Derived Char for Soil Amendment

Soil amendment and carbon abatement by the application of char to soil has attracted attention recently due to concerns over global warming. The term 'bio-char' has been defined as “a form of charred organic material which is applied to soil in a deliberate manner as a means of potentially improving soil productivity and carbon sequestration” [67]. The definition adopted by the International Biochar Initiative (IBI) specifies “the need for purposeful application of this material to soils for both agricultural and environmental gains” [67]. These definitions clearly distinguish bio-char from charcoal, which is used as a fuel for heat or power generation. However, it should be noted that these definitions or the term ‘bio-char’ does not relate to the properties of the material in anyway and is simply used in reference to the application of the char material after it is produced. In addition, these definitions do not specify the feedstock used to produce the char, i.e. biomass, coal or petroleum.

A number of studies have recently reported on the benefits of adding char to soil in terms of carbon sequestration and improved soil productivity [67, 107-110]. However, in most cases the experimental studies were small in scale and limited by a lack of data and geographic location [67]. This underlines the relative infancy of this field of study and the complexity of the experimental tasks [67].

The advantage of applying chars to soil are said to be four fold: long term carbon sequestration, renewable energy generation (if energy is captured during the process), soil amendment (from both productivity and pollution points of view), and waste management / valorization (if waste biomass is used) [67, 108].

Bio-char properties

The process conditions have a significant influence over the char yield and quality (chemical and physical properties) as alluded to earlier. More specifically, the most significant parameters include final temperature, peak temperature, heating rate, pressure, and vapor and solids residence time at final temperature or peak temperature [5, 64, 67, 83, 114, 116, 120].

Activation of bio-chars from conventional and fast-pyrolysis via gasification is a relatively new and interesting area of research. The main areas of importance are, understanding how different processes and operating conditions influence the properties of chars. In particular their influence on texture, porosity, pore structure, fixed-carbon yield and aromaticity; and how these relate to their influence on soil properties, soil processes, soil productivity, moisture retention, cation exchange capability and stability of the char in the soil (carbon abatement) [67].

A key property of char is its apparent biological and chemical stability, which is inferred from studies of charcoal from natural fires and anthropogenic activity, which indicate millennial-scale stability [67]. For this reason, the application of char to soils may result in a net removal of carbon from the atmosphere [67]. However, further work is needed to better understand the stability of chars produced from different processes, reaction conditions and how the properties (chemical and physical) relate to stability.

It is important to note that the relationship between bio-char properties (chemical and physical) and the potential to enhance agricultural soils is still unclear. Similarly, understanding how process conditions may be controlled in order to produce a bio-char with desired characteristics is not complete [67].

Effect of bio-char on plant growth

There is limited information available regarding the effect of bio-char on plant growth [67]. Researchers from the University of Hawaii have been involved in this area since the 1980's and currently have a number of on-going projects to investigate plant growth in greenhouse and field trials [26, 107, 110, 115]. Details of past and recent activities in these areas were the subject of a recent review article [67]. A summary is given below.

Positive impacts of bio-char addition to tropical soils (Hawaii) has been reported for application rates as low 0.5 t/ha on several plant species, whereas application rates greater than 100 t/ha seemed to inhibit plant growth [67]. It has also been reported that an application rate of 11 t/ha significantly improved plant growth for a highly weathered Central Amazonian upland soil fertilized by NPK (in comparison to a control with the same NPK fertilizer rate but no bio-char addition) [67]. The effect of bio-char on soil depends on several factor including soil type, the addition rate and crop type. Further details can be found elsewhere [67, 107, 110, 115].

A key consideration when applying chars from thermochemical treatments of biomass to soils is that although the ash (inorganic) content of the char is relative low from pyrolysis when compared to gasification, the inorganic molecules may be more mobile and in some instances more hazardous to the environmental (depending on the temperature and environment they were exposed to inside the reactor) [95]. Moreover, when comparing chars produced from biomass with those from coal, char from biomass contains less ash than coal derived char; however the ash from biomass is often less stable, more mobile and potentially more harmful to the environment (due to differences in phase composition) [95].

Summary of the energetic, economic and environmental impacts of bio-char systems

Although relatively few LCA have been performed for pyrolysis bio-char systems, a couple of studies have undertaken detailed analyses of energy and emissions associated with bio-char production from conventional pyrolysis [108]. Those studies found bio-char production from energy crops and from crop residues result in net energy production and avoided GHG emissions.

The main findings from the LCA reported in reference [108] can be summarized as:

- Waste biomass streams such as yard waste have the greatest potential to be economically viable while still being net energy positive and reducing GHG emissions.
- Agricultural wastes such as corn stover have high yields of energy generation and GHG reductions, but have moderate potential for profitability, depending on the carbon offsetting cost and feedstock collection cost.
- If energy crops such as switchgrass are grown on land diverted from annual crops, indirect land use change impacts could mean more GHG are emitted than sequestered. Even if switchgrass is grown on marginal lands the economics were unfavorable.
- The primary barriers to the economic viability of conventional pyrolysis to char to soil systems (in general) are the value of carbon sequestration, the cost of the pyrolysis process and the feedstock production and transportation costs.
- The net thermal energy produced by biomass conventional pyrolysis for bio-char applications is 3,000-4,900 MJ/t dry-feed, depending on the feedstock. The amount of carbon dioxide emissions avoided ranges from 0.79-0.89 t CO₂e/t dry-feed for crop-residues and waste biomass. For energy crops, the net emission could be slightly positive or negative depending on indirect land use changes. The most favorable scenario resulted in 0.44 t CO₂e/t dry-feed.

2.4.2.2.5 Summary of pyrolysis for bio-char production

The main issues remaining to be addressed regarding the production of bio-char with application to soil amendment are outlined below, these are a summary of re-occurring points highlighted in the articles cited above [64, 108, 109], and in particular from a recent review article [67].

Further work is needed to better understand the influence of operating conditions on the product (char), particular the peak temperature. Moreover, the influence of the peak temperature on the ‘cation exchange capacity’ and stability in the soil needs to be better understood.

Although conventional pyrolysis is the most common process used to produce bio-char, because of the high char yields obtained, other technologies cannot be underestimated. In this sense, fast-pyrolysis can be an interesting option to co-produce tars (bio-oil) and char at acceptable yields.

Additionally, developing innovative process, such as Flash Carbonization, should be a key priority in order to improve fixed-carbon yields and process efficiency.

Activation of chars should be explored further.

Greater attention should be paid to the characterization and classification of chars using advanced analytical chemistry methods. New 'standard methods' need to be developed for the specific purpose of char application to soil.

Limited information is available on the actual influence of char on plant growth or how the properties of the char effect growth. More work is needed in this area, in particular over long time frames and on large scales (field trials as well as under controlled conditions – greenhouses).

2.4.3 Gasification Platform

Biomass gasification is an energy conversion process producing either syngas (synthesis gas) for the production of liquid fuels and chemicals, or fuel gas for power generation, heat and/or combined heat and power (CHP) applications. Both syngas and fuel gas play important roles as intermediate products in the process.

In the syngas platform, steam or oxygen are used as oxidants. The resulting product gas is enriched in H_2 and CO , which are building block molecules for liquid fuel synthesis. Any raw gas product contains contaminants such as H_2S , NH_3 , HCN , particulate matter, condensable hydrocarbons and alkali species [122]. Consequently, the syngas needs to be cleaned and processed to make it suitable for its intended end use, e.g. Fischer-Tropsch (FT) synthesis. Several processing steps (reforming and shift reactions) can manipulate the syngas composition prior to the FT reactor. The FT synthesis can be realized in different reactor types. Furthermore, off-gas from the FT synthesis can either be recycled partially (full conversion mode) or used directly in a gas turbine for electricity production (once through mode).

When the oxidant in the gasification process is changed to air, the resulting gas, in the term of “fuel gas” or “producer gas”, primarily consists of combustible gases such as CH_4 , H_2 and CO , and incombustible gases such as CO_2 and N_2 . Fuel gas can be used for heat and power generation.

In general, a biorefinery plant based on the gasification (syngas) platform consists of four primary modules, Pretreatment (M_{pr}), Gasification (M_{ga}), Synthesis (M_{sy}) and Upgrading (M_{up}). A biorefinery based on the gasification (fuel gas) platform contains modules comprising of Pretreatment (M_{pr}), Gasification (M_{ga}) and Combustion for power/heat generation (M_{chp}). The Pretreatment (M_{pr}) module has been discussed in the previous section 2.4.1 whereas all others, including unit operations in each module, are described below.

2.4.3.1 Gasification (M_{ga})

During gasification, biomass undergoes several distinct stages including physical changes and chemical reactions such as heating, drying, pyrolysis or devolatilization and char-gas reaction. The following heterogeneous reactions are most commonly involved:

Carbon-oxygen reaction:



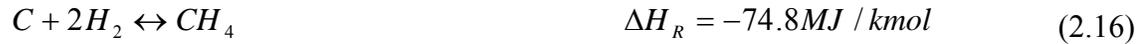
Boudouard reaction:



Carbon-water reaction:

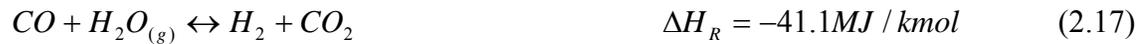


Hydrogenation reaction:



Homogeneous gas phase reactions also influence the gasification process and final gas composition:

Water-gas shift reaction:



Methanation:



For sufficiently long reaction times, chemical equilibrium is achieved and the products are essentially limited to light gases. In practice, this is never achieved in a gasification process and the final gas composition is highly dependent on the reactant ratios (biomass, O₂, and steam) and the reactor temperature.

Gasification is endothermic and requires either simultaneous burning of part of the fuel or an external source of heat to drive the process. Typical product gas compositions [123] for different gasification agents are given in Table 2.31. It indicates that air-blown direct heated (autothermal) gasifiers produce nitrogen-diluted product gas whereas oxygen-blown or indirect heated gasifiers (allothermal) generate product gas with less than 1% nitrogen.

Table 2.31. Typical product gas composition (vol.%) with different gasification agents in biomass gasification [123]

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 ₂ O)	23-28	45-55	<1	10-15	<5
Allothermal (indirectly heated)	Steam (H ₂ O)	35-40	22-25	9-11	20-25	<1

Oxygen-blown gasifiers or steam-blown gasifiers with indirect heating processes are preferred for the purpose for liquid fuel or chemical synthesis, since the syngas contains less nitrogen in the stream. Air-blown gasification is typically used to produce fuel gas for combustion or power generation.

The Gasification module (M_{ga}) consists of three unit operations: air separation, gasifier and syngas processing. Each unit operation may have several options that can be considered for plant design.

U1: Air separation unit (ASU)

An oxygen plant or air separation unit (ASU) is required in an oxygen-blown gasification facility to produce nitrogen free syngas [46, 124].

Cryogenic distillation is the predominant air separation technology that can meet high-throughput and high-purity oxygen demands for gasification. Other available oxygen supply technologies include pressure swing adsorption (PSA), chemical and ITM (ion-transport membranes) processes. However, these technologies are often still in development or are unable to provide sufficient oxygen either for a large scale process or with high enough purity (>95%) for gasification. For instance, the capacity of oxygen production in a PSA ASU plant is normally less than 150 t/d compared with ~3,500 t/d in a cryogenic ASU plant. [125]. For perspective, a 2,000 t/d biomass input gasification plant requires 700 t/d of oxygen [7].

The initial capital cost for ASU can account for up to 15% of the total gasification plant cost and the operating costs are significant due to extensive electricity consumption [126]. A recent report [7] cited \$20-24 million or ~8% of the total installed cost was estimated for an ASU plant built for a biomass gasification system with 2,000 dry tonne per day input. Furthermore, the ASU is the largest consumer of power in the overall process. In the high temperature scenario ~24% (11.6 MW) of the gross power production (48.6 MW) in the plant is consumed for oxygen production [7].

Air-blown gasification is unlikely to be technically and economically competitive with oxygen-blown gasification system, because nitrogen would be present in the product gas and would remain in the following synthesis reaction system. Additionally, it would lead to lower thermal efficiency, higher gas compression energy requirements, larger downstream equipment sizes, etc. Also, nitrogen can form ammonia and other potentially harmful nitrogen compounds in the downstream synthesis units.

U2: Gasifier

Gasifiers are usually classified into three main types that are suitable for biomass gasification: fixed-bed or moving bed gasifier (Figure 2.38), fluidized-bed gasifier (Figures 2.41-42) and entrained flow gasifiers (Figure 2.41).

As gasification is an endothermic process, thermal energy has to be provided to drive the reactions. The autothermal (as shown in Figures 2.40, 2.41 and 2.43) gasifiers generate heat by

partial feedstock combustion and allothermal gasifiers (as shown in Figure 2.40) require an external heat source.

U2-A: Fixed-bed (moving bed) gasifier

Figure 2.38 shows the two types of fixed-bed gasifiers: updraft and downdraft. 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 one of the main problems for a small scale industrial application.

Updraft gasifiers are characterized by biomass entering the top of the reactor and air/oxygen/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 as shown in Figure 2.38-a. In this reactor, tars form at a level of up to 100 g/Nm³ [127]. 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. Fuel particle size limit, a high tar yield and the potential for slagging [5] are noteworthy disadvantages.

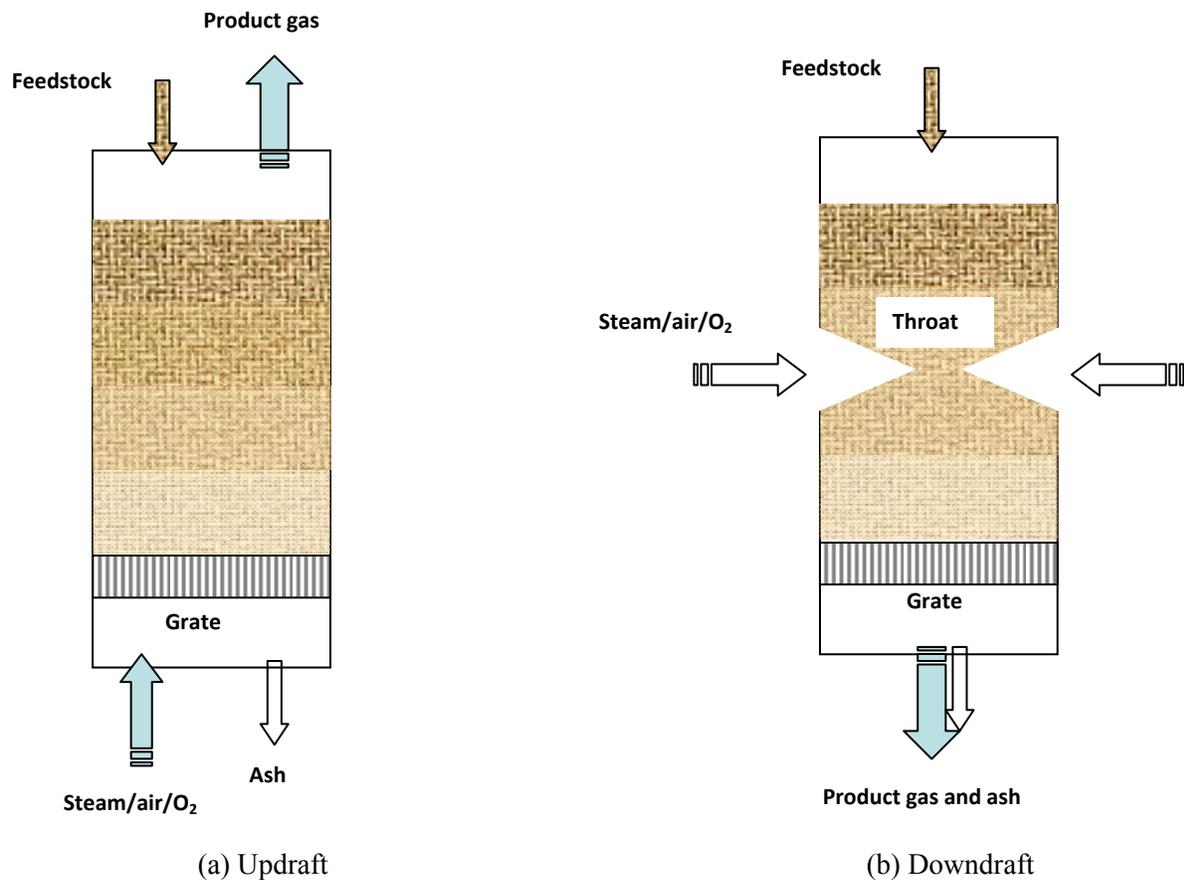


Figure 2.38. Two types of fixed-bed gasifiers: updraft and downdraft

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 as depicted in Figure 2.38-b. In this gasifier, 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/Nm³). 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, and difficulties in handling biomass with higher moisture and ash content [5].

Commercial fixed bed gasifier manufacturers [128] include Lurgi Dry-Ash Gasifier, and BGL Gasifier, that were initially designed for coal gasification but were modified for using biomass.

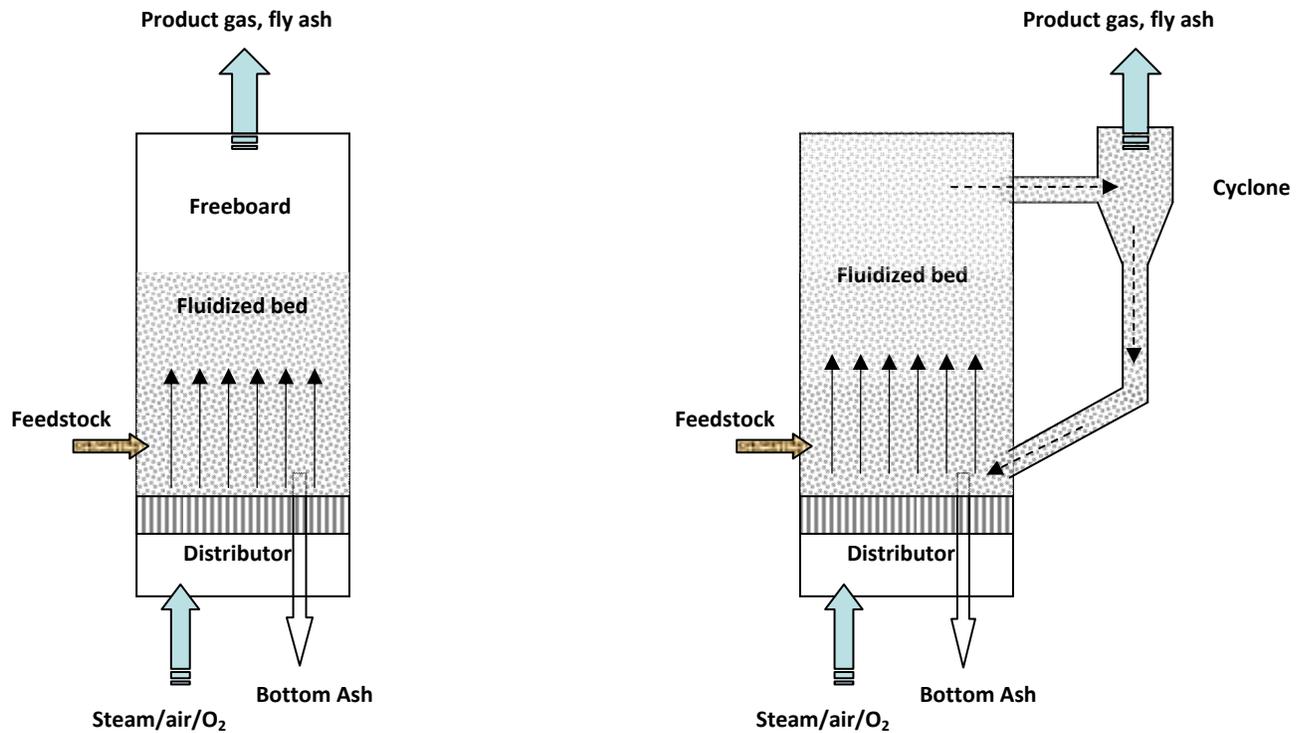
For small and medium scale gasifier systems, an inventory of US manufactures can be found in a NREL technical report [129].

U2-B: Fluidized-bed gasifier

In a fluidized-bed gasifier, biomass fuels with particle sizes up to 10 cm, air/oxygen, and/or steam enter at the bottom of the reactor. The velocity of the gas stream forces the biomass upward through a heated inert bed of fluidized ceramic or silica particles. In general, fluidized bed gasifiers accept a wide variety of feeds, and the operating temperature should be lower than the ash melting temperature of fuel, commonly between 700°C and 1100°C. This type of gasifier produces considerable amounts of tar and aromatics, which makes extensive gas cleaning necessary. The typical tar concentration is 10 g/Nm³ and lying in the range between the updraft and the downdraft gasifier [127]. Fluidized bed gasifiers are best suited for large-scale applications of up to several hundred MW_{th} fuel input. Figure 2.39 schematically shows two types of fluidized-bed gasifiers: (a) a bubbling fluidized-bed gasifier (BFBG) and (b) a circulating fluidized-bed gasifier (CFBG).

Fluidized-bed gasifiers have proven to be reliable at both pilot and commercial scales. BFBG (Figure 2.40-a) are more economic for small to medium range (1-10 MW_{th} fuel input) capacities, whereas CFBG (Figure 2.40-b) are very reliable for a variety of fuels and are relatively easy to scale up to 100 MW_{th} fuel input [130].

Pressurized reactors can increase the capacity and can benefit an integrated combined cycle (such as IGCC, and F-T synthesis) as the need to compress the product gas in the combustion chamber of a gas turbine or in a synthesis reactor. However, pressurized systems incur additional capital costs.



(a) Bubbling fluidized bed gasifier

(b) Circulating fluidized bed gasifier

Figure 2.39. Two types of fluidized-bed gasifiers

Fluidized bed gasifiers are commercially manufactured [131] by HTW (High Temperature Winkler), KBR Transport Gasifier, Great Point Energy, U-GAS, etc. Most of them are currently designed and extensively used for coal gasification. For small and medium scale biomass gasification systems, a number of the US companies can be found in the NREL report [129].

U2-C: Twin-bed fluidized-bed gasifier

A twin fluidized-bed, indirectly-heated gasifier system, as shown in Figure 2.40, consists of a fluidized-bed combustor and a fluidized-bed gasifier. In this coupled system, biomass is reacted with steam in the gasifier and char is reacted with air in the combustor. Thermal energy is provided to the gasifier by circulating hot sand from the combustor. Char, together with sand (bed material), is circulated to the combustor, where char and any other carryover gas are burned using air [132]. As a result, sand is circulated between the two reactors providing heat transfer

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.

The Battelle gasification process, demonstrated at the McNeil power plant in Burlington, Vermont, is a typical example that uses an indirectly heated gasifier to produce syngas from biomass. The primary fuel gas is of medium calorific value with a HHV of 17.75 MJ/Nm³ [133]. A commercial plant [134] was reported to operate since 2003 in Gussing, Austria. This biomass CHP plant has a capacity of 8 MW_{th} fuel input and 2 MW electricity combined with 4.5 MW thermal outputs.

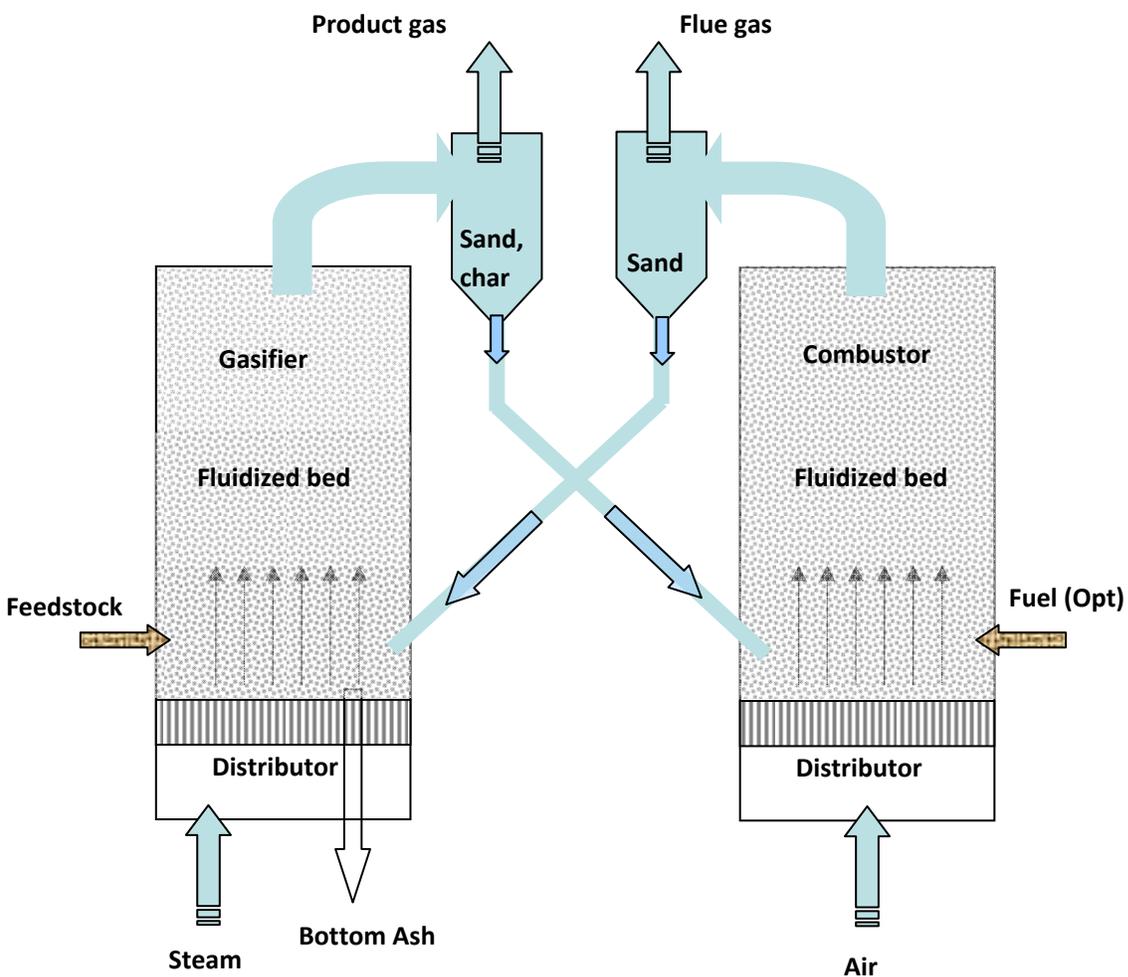


Figure 2.40. Indirectly heated fluidized-bed gasifier (allothermal)

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. Compared with the other gasifiers, a twin-bed gasifier is more complex to build [135], but can realize a higher energy conversion efficiency [136].

U2-D: Entrained Bed Gasifier

The entrained flow gasifier, as shown in Figure 2.41, 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 [35, 65]), entering with oxygen and steam at the top of the gasifier.

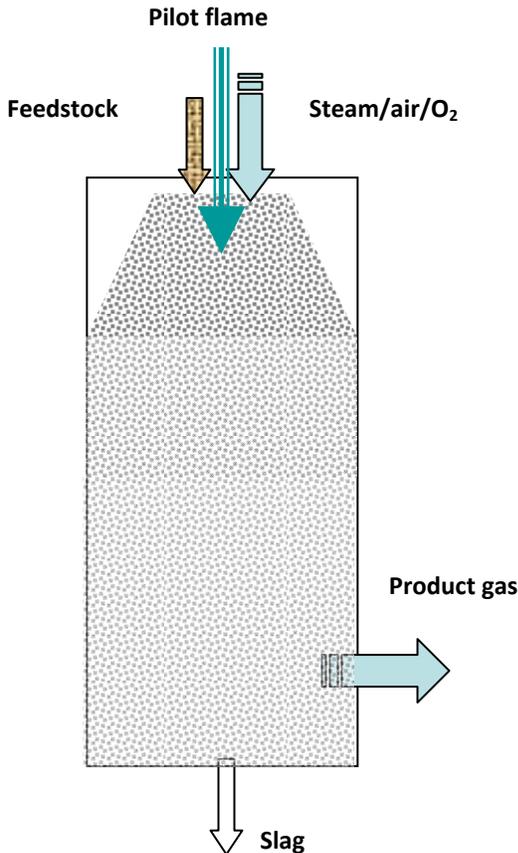


Figure 2.41. Entrained flow gasifier

Typically, the entrained flow gasifier is operated at high pressure (up to 100 bar) and high temperature (up to 1200°C or even higher) and completely convert fuel into syngas, even at short

(a few seconds) residence times. An external pilot flame may be required to increase temperature and to facilitate reactions. Under these conditions, the syngas contains very low level of tar and methane, which simplifies gas cleaning and increases efficiency for the subsequent synthesis process.

The entrained flow gasifier can be used for biomass feedstock with low ash melting point. Adding fluxing material, such as limestone or other Ca-rich material can enhance ash conversion to molten slag at the operating temperature. Molten slag condenses and forms a solid protective layer on the inner wall of the gasifier. Subsequent slag remains in liquid form, flowing down and exiting at the bottom of the gasifier [132].

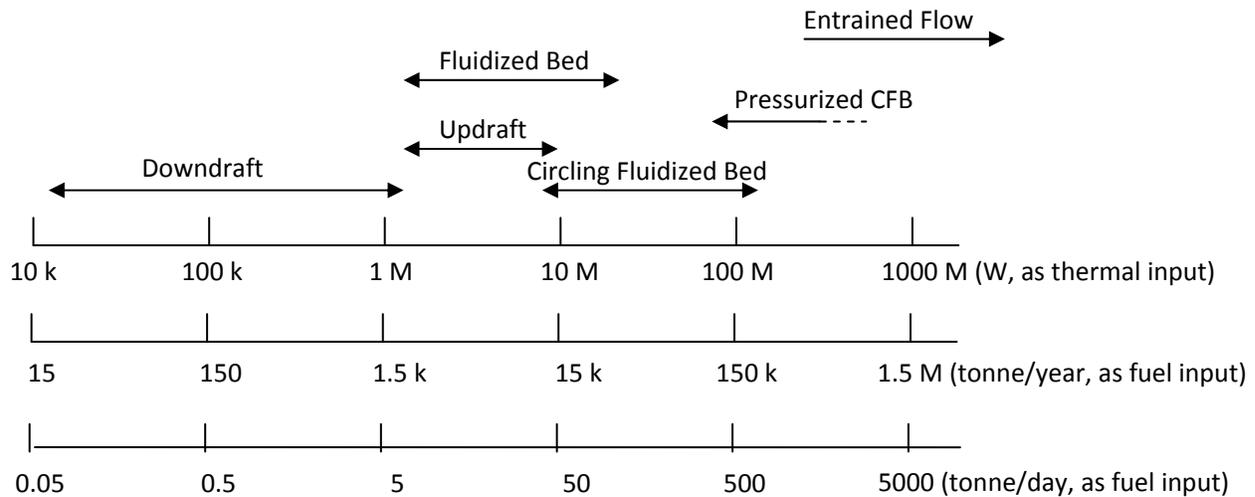
In comparison to fixed-bed and fluidized-bed gasifiers, an entrained flow gasifier is capital intensive and calls for large scales to take advantage of “economy of scales” and hence, limit the production costs. Therefore, entrained flow gasifiers are considered economical in large scales up to 1000 MW_{th} fuel input.

Manufactures of slagging entrained flow gasifiers include Shell, GE (former Texaco), Krupp-Uhde, ConocoPhillips (E-GasTM), Siemens, MHI (Mitsubishi Heavy Industries), Huaneng Clean Energy Research Institute (HCERI), etc. Most of them are designed for coal gasification but can be modified to use biomass as fuel [128].

Gasifier type and capacity

There is an approximate relationship [137] between the gasifier type and the scale that gives the lowest cost (economy of scale), as shown in the Figure 2.42. For a large scale application (up to hundreds MW_{th} fuel input), the preferred and most reliable system is the pressured circulating fluidized bed (PCFB) gasifier or entrained flow gasifier. For small-scale applications (<10 MW_{th} fuel input), the fixed bed gasifiers (updraft and downdraft) and bubbling fluidized-bed gasifiers are better suited. Circulating fluidized bed (CFB) gasifiers can be competitive in medium scale (10-100 MW_{th} fuel input) applications. Another option for a large scale application is to operate a group of small scale gasifiers in parallel, e.g. Great Plains Synfuels Plant (North Dakota) ran 14 Lurgi gasifiers (fixed bed type) for total 14,500 t/d (16,000 ton/day) of coal [52]. In addition, pressurized gasification system can increase the process capacity and energy efficiency

compared with atmospheric systems. Based on Aspen® process evaluation, it has been reported that pressurized operation can increase the overall LHV (low heating value on wet basis) energy efficiency by ~10% [138].



Assumption for calculation:

1. Biomass typical high heating value (HHV): 18 MJ/kg
2. Gasifier operation days per year: 80% of 365 days

Figure 2.42. Gasifier technologies vs scale (as fuel input) (adapted from reference [137])

U3: Syngas processing

Along with H₂, CO, CO₂, and CH₄, syngas contains fine particulate matter, C₂+ gaseous hydrocarbons, heavier condensable hydrocarbons (benzene and higher molecular weight compounds) that are collectively termed “tar” and gaseous containments such as HCl, H₂S, NH₃, HCN, as well as alkali metals that are vaporized during thermochemical reactions from compounds present in the biomass feedstock. These contaminants are potential threats to catalysts and require removal prior to subsequent synthesis reactions. In addition, CO₂ as one of the by-products in gasification, often needs to be removed prior to the syngas entering the compressor and pressured synthesis reactors.

The following unit operations are typically or selectively integrated in a gasification platform for generating syngas or fuel gas. The importance of removing a specific contaminant depends on the end-use of the product gas.

U3-A: Particulate matter removal

Particulate matter in the product gas consists of fuel ash, dust, unconverted carbon and carry-over bed material in the case of fluidized bed gasifiers [132]. Many different technologies, such as cyclones, barrier filters, bag filter, electrostatic filters, wet scrubbers, etc. have been used to remove particulate matter from fuel gas.

Cyclones are usually selected as the initial step for particulates removal in most gasifier systems as they are effective and relatively inexpensive to build and operate [139]. In circulating fluidized bed gasifiers, cyclones are an integral part of the reactor design providing for separation of the bed material and other particulates from the gas stream. Separation efficiency can be improved by up to 90% for the $> 5 \mu\text{m}$ particulates by using multiple units in series (multi-clones) but are less effective for particulates smaller than $5 \mu\text{m}$ [139, 140]. This technology is commercially mature and is extensively used in industrial processes.

Barrier filters [139] such as rigid or porous candle filters or cross-flow filters constructed from metal or ceramic material have been used as an alternative method for particulates removal from product gas. The barrier filters are usually placed downstream from cyclone filters to remove smaller particulates (effective for the particulates from 0.5 to $100 \mu\text{m}$ in diameter). However, barrier filters have technical and economic constraints for removing particles smaller than $\sim 0.5 \mu\text{m}$. Additional problems are related to the operating conditions that can cause sintering and corrosion of metal filters and plugging or mechanical failure of ceramic filters [7, 139]. Ceramic and metal candle-type filters have been tested successfully at gasification demonstration facilities [139].

Bag filters [139] are constructed of woven materials that are suitable for operation at low temperature up to 350°C . The low operating temperature requires the hot syngas to be cooled prior to filtration, and may cause plugging problems should tar compounds condense onto the filter bag surface. Packed-bed filters [139] may act as a type of barrier filter, in which the raw

product gas passes through a bed of packing material such as ceramic spheres, sawdust or activated carbon that disengage particulate matter from the gas stream. Packed-bed filters can be used in a small-scale gasifier facility to remove both particulate matter and tar from the gas stream. The accumulation of particulates and tar in the packed bed can lead to higher pressure drops across the filter and associated operating problems.

In electrostatic filters [139], the particulate matter in the gas stream is electrically charged by high voltage electrodes and subsequently removed from the gas stream by collecting on oppositely charged collector plates. Particulate matter can be scrubbed from the collector surface by either wet or dry methods. Dry scrubbers can operate at temperatures of 500 °C or more and wet scrubbers are limited to temperatures of about 65 °C as they are often using flowing water.

Electrostatic filters are reported to be used in updraft fixed-bed gasifiers for producing clean fuel for gas engines in Germany and Denmark [139]. The facilities have electrical generation capacities of about 3.5 and 1.0 MW_e, respectively. In the German facility, the gas stream is first cooled and then passes through a cyclone, a catalytic tar cracker, and an electrostatic precipitator (dry) for further particulates removal. In the Denmark facility, the system does not have a tar cracker and the cooled gases pass from the cyclone directly into a wet electrostatic precipitator for further particulates removal. Electrostatic filters have been used in many coal-fired power stations, biomass combustion facilities, and in a few small scale gasifiers [139].

Wet scrubbers use water sprays to remove particulates. The most common wet scrubbers use a venturi design to create a pressure drop that allows water to be easily sprayed into the gas stream. With pressure drops of between 2.5-25 kPa, these scrubbers can remove 99.9% of particles over 2 μm, and 95-99% of those over 1 μm [140]. To reduce carry-over of water into the gas phase, the producer gas needs to be cooled before scrubbing. Most biomass gasification systems currently use wet scrubbers to remove tars rather than particulates from the gas stream. However, scrubbers cause a loss of sensible heat, which may be undesirable in some systems.

U3-B: 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 the main technical barrier in the biomass gasification process [127].

The main methods used to eliminate tar include wet scrubbing, wet electrostatic and catalytic reforming.

A wet scrubbing system usually consists of a venturi scrubber and a quench chamber. The use of water in these scrubbers requires the gas temperature at the exit to be in the range of 35-60 °C [139]. Simple water scrubbing may not be always effective at removing tar and results in the accumulation of tar in the scrubbing water so that additional waste water treatment is required. Instead of water, organic washing liquids can be used for gas clean, e.g., “OLGA” tar removal technology [141], developed by ECN (Energy Research Center of the Netherlands).

Wet scrubbers are commercially mature technologies and have been extensively used for gas processing in the coke-making industry [139]. However, they have not yet been proven to be reliable in biomass gasification system on either an operational or cost basis.

Wet electrostatic precipitators are very efficient at removing either tars or particulates from the gas stream and can remove up to 99% of materials under 0.1 μm in diameter. The working temperature is about 150 °C, but would likely be lower for tar removal to avoid tar vaporization. This technology is mature and available commercially for a variety of applications. However, the high capital and operating costs are the primary barriers for the use of these systems with large scale biomass gasifiers [139].

Catalytic reforming is a preferred treatment method because it converts harmful tar compounds into additional CO and H₂. NH₃ may also be decomposed in this step. The efficiency of tar conversion (elimination) depends on the properties of the catalyst used, space velocity, reaction temperature, and composition of the reacting flow, particularly H₂O and CO₂ contents in syngas. Commercial tar-cracking catalysts (Ni-based) have been shown to reduce tar effectively through

reforming reactions with steam and CO₂, but they are expensive and easily deactivated by coke formation, H₂S -poisoning and sintering at high temperatures [101, 142].

U3-C: Sulfur and other gaseous impurities removal

Under the reducing atmosphere of gasification conditions, H₂S is the primary sulfur species produced when sulfur is present in the biomass feedstock. Minor amounts of carbonyl sulfide (COS), and thiophene (C₄H₄S) are also formed. These gaseous sulfur compounds deactivate catalysts used for tar cracking and the water-gas shift (WGS) reaction in downstream reactor units.

Zinc oxide (ZnO) is the most commonly used sorbent for H₂S removal because of its favorable sulfidation thermodynamics. The removal of H₂S is accomplished by reacting ZnO and H₂S to produce ZnS and water.



Ammonia (NH₃) is the most significant species from fuel nitrogen conversion in biomass gasification and is a precursor to NO_x emissions in downstream burners, gas engines, or gas turbines. NH₃ can be removed by wet scrubbing processes or catalytic conversion [139]. Ni-based tar-reforming catalysts operating at ~800°C have been shown to effectively remove NH₃ from gasifier product gas [101, 139].

The other trace contaminants, including cyanide and chloride compounds, may also cause corrosion and act as catalyst poisons. Hence, efficient removal may be required.

U3-D: Alkali removal

The mineral matter in biomass may contain high levels of alkali metals, principally potassium (K), that are released as alkali salts, principally KCl, during the gasification process. Alkali vapors will remain as a vapor in hot gases and deposit on cold surfaces downstream or condense onto particulate matter. Alkali removal from the gas stream is therefore important in some critical applications such as gas turbines [139].

Alkali vapor can be removed by cooling the product gas below 600 °C to allow for alkali condensation onto the 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 heat that may reduce system efficiency. Alkali “getters” [143], a packed-bed filter loaded with sorbent material, may be an effective method to remove alkali from the gas stream at high temperatures (650-725 °C).

U3-E: CO₂ removal

A number of technologies are available for CO₂ removal including chemical solvents, physical solvents, mixtures of physical / chemical solvents and membranes.

The two most applicable technologies are using chemical solvents and physical solvents. Chemical solvents, such as methyldiethanolamine (MDEA) and diethanolamine (DEA), have high absorption capacity at relatively low CO₂ partial pressures. Physical solvents, such as dimethyl ethers of polyethylene glycol, are favored at high CO₂ partial pressures. The SELEXOL® process is a physical absorption technology from UOP, which has been commercially used for removing acid gases (CO₂, H₂S, etc.) from natural gas and syngas streams [144].

When the syngas contains significant concentrations of other gases besides H₂ and CO, adsorption on solid sorbents is preferred. The effective sorbents include silica gel, activated carbon, zeolites, and molecular sieves. The adsorption takes place at low temperatures and high pressures and the regeneration takes place either by higher temperature (TSA: Thermal Swing Adsorption) or lower pressure (PSA: Pressure Swing Adsorption) [132].

2.4.3.2 Synthesis of Liquid Fuels and Chemicals (M_{sy})

After cleaning, syngas is compressed to 20-200 bar (depending on the synthesis conditions) before downstream synthesis [123]. In principle, if clean syngas is produced from biomass, there

should not be any serious technical barrier for its subsequent conversion to methanol, ethanol or Fischer-Tropsch (F-T) liquid products as these processes have been demonstrated or commercialized by Shell in Malaysia and SASOL in South Africa.

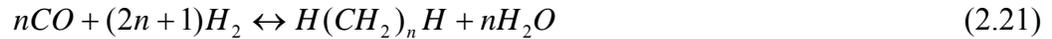
UI: Fischer-Tropsch Synthesis

F-T synthesis refers to processes for the conversion of synthesis gas to syncrude. The main reactions during the F-T synthesis process can be represented by equations 2.20-2.25: [145]

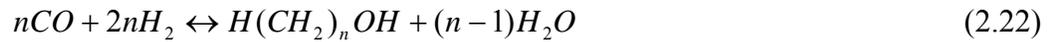
Alkenes:



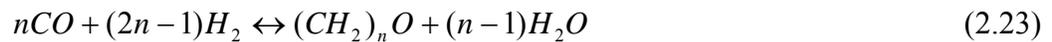
Alkanes:



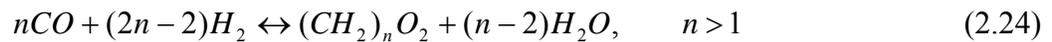
Alcohols:



Carbonyls:



Carboxylic acids:



Water gas shift:



Two types of synthesis processes that are operated at different temperatures can produce different products. In these processes, catalysts and operating pressures may be different [146].

(1) High temperature FT Synthesis (HTFT). The typical HTFT process is performed at temperatures between 300 and 350°C and pressure of 20-40 bar. Iron catalysts are widely used and the products mainly contain “light” hydrocarbons that can be used for the production of materials that are usually made from petrochemicals (ethylene, propylene, etc.).

(2) Low Temperature FT Synthesis (LTFT). The typical reactions take place at temperatures of 200-250°C and pressures below 20 bar. Iron and cobalt catalysts are commonly used in the process. The main products have higher boiling points and are suitable for diesel production.

FT synthesis generates a distribution of products that depends on the catalysts and the reaction conditions. Table 2.32 lists two F-T synthesis product distributions at different temperatures using Fe-based catalyst [146].

The collective set of synthesis reactions are very exothermic and can only be operated in a relatively narrow temperature range. This imposes stringent demands on both heat removal and temperature control. The raw synthesis products (syncrude) can be further refined to transportation fuels and chemical products in conventional petroleum refining processes.

Table 2.32. FT products distribution for Fe-catalyst (per 100 carbon atoms) [146]

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	18	36
Middle distillate	19	12
Heavy oil and waxes	48	9
Water soluble oxygenates	3	6

There are three types of reactors that have been applied commercially or are considered suitable for commercial application. These reactors are the gas/solid (two phase) fluidized bed reactor,

the multi-tubular fixed bed reactor and the three phase slurry reactor [147]. However, there is not sufficient background information to prefer one reactor over the other without comparison of the performances of optimized reactor and catalyst combination [147].

The fluidized bed and the three phase slurry reactors have been applied extensively by Sasol, and the multi-tubular fixed bed reactors developed by Shell. The main advantages of the multi-tubular fixed bed and three phase slurry reactors are listed and reproduced from [147]:

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.

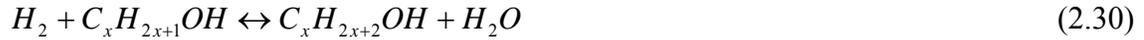
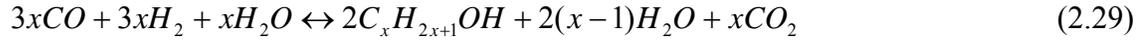
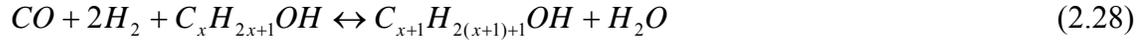
Three phase slurry reactor:

- 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.

U2: Ethanol and higher alcohols production

Mixtures of C₂-C₆ alcohols can be catalytically produced from syngas. The main synthesis reactions are listed below [8]:





The catalytic reactions of syngas to alcohols are typically performed in a fixed-bed or slurry reactor. Alcohols selectivity is in the range of 70-80 wt%, and ethanol concentrations are reported as 34.5 wt% and 46.1 wt% by Dow and SRI International, respectively [148]. The reactions are highly exothermic and require heat removal to maintain suitable operating temperatures.

The mixed alcohols are synthesis products, which need to be de-gassed, dried and separated into ethanol and higher alcohols [8, 148]. First, the mixed alcohols are separated from the off-gas in a flash separator. The off-gas stream, which contains CO₂ and a small quantity of hydrocarbons and alcohols, can be recycled to the synthesis reactor. The mixed alcohol stream is depressurized and then dehydrated using a molecular sieve. The resulting dried alcohols are sent to a main distillation column, where 99% of the incoming ethanol and methanol is recovered overhead, and low boilers such as propanol, butanol and pentanol remain in the bottom stream. The overhead stream can be further processed in a second distillation column to obtain a high purity ethanol product.

He et al. [8] published a techno-economic assessment for a biomass-to-ethanol process based on an energy self-sufficient syngas platform (no natural gas or electricity purchased). The mass and energy balances for each process and unit were evaluated, and it was determined that for the production of 1 kg (or 1.27 L) ethanol, 4 kg of dry biomass and 3.3 kg of fresh water were required.

U3: SNG (synthetic natural gas) production

The syngas from gasification can be used to produce SNG (synthetic natural gas) by methanation reactions. In this process carbon monoxide and hydrogen react to form methane and water, as outlined below.



Typically, nickel oxide catalysts promote the high pressure (20-30 bar) exothermic reactions [132].

2.4.3.3 Upgrading (M_{up})

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 [149]. In a typical FT product distribution, as listed in Table 2.32, it is found that nearly half of the total amount of products is heavy oils and waxes.

The upgrading of the heavier products is mostly carried out using catalysts such as Pt, Pd, or bimetallic systems like Ni/Mo, Ni/W, Co/Mo in their sulfided forms supported to substrates such as oxide mixtures, zeolites or silicoaluminophosphates [149]. The catalysts are normally designed as bi-functional in 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 products from the upgrading reactors can be used to generate power in a combined cycle system.

2.4.3.4 CHP (Combined Heat and Power) (M_{chp})

Low or medium heating value fuel gas (5-6 MJ/m³) is produced from air-blown gasification and can be used in “combined heat and power” (CHP) applications. Typically, CHP systems include reciprocating or combustion turbine engines or steam turbines to generate electricity. A heat exchanger recovers waste heat from the engine and/or exhaust gas to produce hot water or steam, which can be captured and utilized for domestic or industrial purposes. Typically one-third of the total energetic output is electricity and two-thirds heat [132]. Compared to producing the electricity and process heat separately, CHP process can reduce fuel consumption by 10 to 30% for the production of an equivalent amount of electric power and heat [146, 150].

The capital cost for power plants based on biomass gasification in the United States is about \$2,000-\$3,000/kW_{el} and generation cost is in the order of \$90/MWh_{el}. Such plants may be cost-effective in CHP mode if connected to district heating schemes. In Europe, the investment cost of biomass plants varies considerably from \$1,000 to \$5,000/kW_{el}, depending on plant technology, level of maturity and plant size [151].

2.4.3.5 Techno-Economic Analysis

FT synthesis

Chemical synthesis based on coal gasification technology has been widely applied in the chemical industry to produce chemical intermediates and fertilizers, i.e., synthesis of ammonia and urea, as well as town gas, hydrogen, etc [132]. It is anticipated that experience gained from coal operations can be transferred to solve problems related to biomass use. However, some technical barriers related to biomass characteristics still need to be extensively studied to attain a high degree of reliability for the biomass gasification process.

FT synthesis for liquid fuels and chemicals based on the gasification platform is technically feasible. Many coal-to-chemicals processes have shown that the integration of gasification, cleaning, reforming, and synthesis is possible. System economics are related to availability and

supply of feedstock, the plant scale and technical risks. All these variables lead to a number of possible process configurations and different technology selections at different capacities. Compared to fossil fuels, the biomass supply and transportation in most places are a challenge. To avoid this challenge and improve economic feasibility, it is important to size plants to match the local biomass resources and produce intermediate products such as bio-oil, which can be subsequently upgraded at a central facility [132]. Furthermore, the competitiveness of future biomass FT production strongly depends on the evolution of a biomass market, ongoing technology development and optimization of the system configuration.

A wide range of scales is reported for FT synthesis plants [132] 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 per day (i.e. $\sim 1,000$ MW_{th} fuel input), while a new plant in Qatar has a capacity of six times higher with 75,000 bbl per day of liquid fuels production ($\sim 6,000$ MW_{th} as fuel input). A plant size of $\sim 1,000$ MW_{th} seems to be a typical size and would require about 5,000 tonnes of dry biomass daily. However, a smaller scale FT plant (100–200 MW_{th} biomass input) was also mentioned by Hamelinck et al. in 2004 [152], indicating that the produced FT diesel could be competitive with fossil diesel in the case of tax exemption in Europe.

Tijmensen [138] 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. [152], who estimated the total capital investment cost of a similar scale plant (400 MW_{th} fuel input) with €286 million in 2004. Hamelinck's plant included a 25 bar oxygen-blown gasifier, a tar cracker, wet gas cleaning and a solid bed F-T reactor with 70% conversion in once-through conversion mode. In such 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 HHV basis. Production cost of FT liquids were estimated as 16 €/GJ or 2.45 €/Gal (\$2.16/Gal in 2002). Table 2.33 lists the influence of scale on the costs of investment and FT fuel products based on the plants with 80, 400, 1,000, and 2,000 MW_{th} fuel input [152].

Table 2.33. The FT synthesis plant scale and relevant cost estimates (quoted and adapted from reference [152])

Capacity, MW _{th}	Fuel input, tonne/ 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

Assumption 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} = 86400 MJ/day, then
Input (kg/day) per MW_{th} capacity = 86,400 (MJ/day)/18 (MJ/kg) = 4800 kg/MW_{th}
5. For 400 MW_{th} input FT plant:

$$\begin{aligned}
 \text{biomass input} &= 4800 \text{ kg/day/MW}_{\text{th}} \times 400 \text{ MW}_{\text{th}} \\
 &= 1920,000 \text{ kg/day} \\
 &= 1920 \text{ tonne/day}
 \end{aligned}$$

A biomass FT synthesis plant with a scale of 741 MW_{th} (LHV) input (~4,000 tonne per day biomass input) was analyzed in 2011 by Reichling et al [153]. The process was optimized for electricity generation and an output of 253 MW_{th} (LHV) FT liquids and 171 MW electricity are reported with an overall efficiency of 57.2%. Cost estimates range between \$430-590 million and comply with values listed in Table 2.33 [153].

A techno-economic analysis report [7] from NREL by Swanson et al. represents the most likely current (2010) state of biomass FT synthesis. The report compares the capital and production costs for two temperature scenarios, LT scenario and HT scenario, based on a gasification platform and a 2,000 t/d corn stover feed rate. The gasifier selected in the LT scenario is an oxygen-fed, low-temperature (870°C), non-slugging, fluidized bed gasifier. The HT scenario is based on an oxygen-fed, high-temperature (1,300°C), slugging, entrained flow gasifier. The

syngas from the gasifiers is used for FT synthesis, hydro processing and electricity production in both scenarios. The energy balance and mass flow rates are listed in Table 2.34.

Table 2.34. Overall mass flow and energy balance in the scenarios of biomass-to-fuels based on gasification [7]

	HT Scenario	LT Scenario
Input, tonne/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

The total capital investment required for the nth plant scenarios has been reported [7] as \$610 million for the HT scenario and \$500 million for the LT scenarios. Product value (PV) for the HT and LT scenarios are estimated to be \$4.30 and \$4.80 per gallon of gasoline equivalent (GGE), respectively, based on a feedstock cost of \$82 per dry tonne.

Table 2.35 summarizes the cost analysis from various sources. It can be concluded that cost estimates vary greatly depending on the underlying assumptions, the level of technological development and plant size [7]. However, the product value seems to fall into a narrow range of 12-16 \$/GJ.

Table 2.35. Comparison of techno-economic studies of biofuel production plants based on biomass gasification

	Williams et al. [154]	Phillips et al. [148]	Tijmensen et al. [138]	Larson et al. [155]
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. [8] performed an economic analysis for a biomass ethanol synthesis plant. 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 decrease with increasing plant scale [8].

The capital investment in a biomass ethanol synthesis plant can be broken down into pretreatment, gasification, gas cleaning including tar/CH₄ reforming, alcohols synthesis, alcohols separation and purification, power generation and utilities. The biggest share of capital investment was allocated to syngas 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 [8].

3. Integrated Biorefineries

3.1 Biomass Resource Potential in the State of Hawaii

3.1.1 Terrestrial Biomass

Biorefineries in the State of Hawaii will be established as one component in a bioenergy/biofuel value chain as depicted in Figure 3.1.



Figure 3.1. Illustrative example of bioenergy/biofuel value chain components.

At least two assessments of biomass resources have been completed for the State of Hawaii over the past 10 years [16, 156]. Both reports identified existing biomass resources generated by sugar plantations and the biogenic fraction of municipal solid waste stream (MSW) in the Honolulu urban area as the largest biomass resources aggregated at single locations in the State. Although two very different resources, both sugarcane and MSW have highly developed collection systems that have evolved in response to market forces and government policy. The two reports also touched on energy crop production systems. The potential for the production of sugarcane, trees, and algae to support bioenergy development was the focus of two additional reports [157, 158]. Building upon this, the Hawaii Bioenergy Master Plan further explored the issues of risk and barriers to bioenergy/biofuel value chain development. The current assessment of biorefineries suitable for deployment in Hawaii must thus necessarily be cognizant of value chain constraints. While it appears that market demand for competitively priced, drop-in replacements for diesel, jet, motor gasoline, or liquid boiler fuels far outstrips any near term supplies, the markets for fuels that are blended to overcome fuel system compatibilities (e.g.

ethanol) are more limited. Thus distribution and end use downstream of the conversion facility (Figure 3.1) is perceived to be a lesser constraint than cost effectively generating adequate supplies of biomass feedstock and aggregating them at a conversion facility. The suitability of various biorefinery options for Hawaii thus largely depends on how well the required scales of the biorefineries match with the anticipated scales of feedstock supply.

Based on the results from successful trials, the most promising crops for fiber production include the grass crops *Saccharum officinarum* (sugarcane) and *Pennisetum purpureum* (banagrass) as well as the woody crops *Eucalyptus sp.* (*Eucalyptus*), and *Leucaena leucocephala* (giant *Leucaena*). Other crops such as corn, sweet sorghum, albizia, guinea grass, etc. have been proposed but large-scale trials to evaluate their suitability as energy crops have not been carried out on Hawaii [55, 157].

Within the framework of assessing the biomass-based ethanol production potential for the State of Hawaii, Keffer [10, 157] evaluated the spatial distribution of soil types, zoning and annual rainfall using geographic information system (GIS) technology. Suitability for a specific crop was established by matching land characteristics (annual rainfall, soil type and slope) with growth requirements for a crop. The selection of suitable land was further reduced by applying zoning criteria and land ownership restrictions. Sugarcane, banagrass, *Eucalyptus* and *Leucaena* were selected as potential ethanol feedstock crops, respectively, based on historical crop production in Hawaii or energy crop research trials. It was further assumed that tree species, *Leucaena* and *Eucalyptus*, would be grown without applied irrigation, that *Leucaena* was suitable for drier locations (20 to 40 inches), and that *Eucalyptus* was suitable for the areas receiving more than 40 inches of annual rainfall.

Acreage for each land category and crop type is summarized in Table 3.1.

Table 3.1. Available land based on five land groupings and two crop scenarios, acres [10]

Land suitable for:	Land groups	Total Zoned Ag ^a	Zoned Ag, state owned	Zoned Ag, large land owners
Cane, corn, cassava, banagrass		360,000 ^b	51,000	252,000
Trees (<i>Eucalyptus</i> , <i>Leucaena</i>)		699,000	160,000	491,000
^a Ag = agriculture ^b all numbers are rounded to nearest 1,000 ^c acreages are not mutually exclusive				

Keffer’s report [10, 157] assumed that soil types adequate for sugarcane farming were also suitable for banagrass production. In addition, soils suitable for sugarcane that had adequate rainfall were also assumed to be capable of growing *Eucalyptus* and *Leucaena*. The present work further assumes that sugar soils could also support corn and cassava. As a result of this approach, the acreage values in Table 3.1 are not mutually exclusive, i.e. the same physical acre may be included in multiple classifications.

While the land categories in Table 3.1 illustrate the State’s potential to produce biofuels and electricity from locally grown energy crops on agriculturally zoned land, it does not speak to the rationality of such an undertaking. Although locally grown energy crops are important for Hawaii’s energy independence, growing food, providing pasture for grazing animals and maintaining ecological diversity and scenic beauty are of great importance as well.

3.1.2 Aquatic Biomass

Land suitable for growing photoautotrophic microalgae in the State of Hawaii in open ponds was also assessed using GIS software as summarized in Table 3.2. Assumptions are summarized immediately below the table [158]:

Table 3.2. Land areas suitable for open-pond, phototrophic algae plantation [158]

Island	Kauai	Oahu	Molokai	Lanai	Maui	Hawaii	Total
Land, acres	8,840	24,295	12,650	7,938	26,799	36,638	117,160
<p>Criteria:</p> <ul style="list-style-type: none"> • Rainfall < 40 inches per year: Algae production facilities should receive no more than 40 inches of rain per year to minimize the dilution of algae stock in open ponds; • Solar insolation ≥ 400 cal/cm²/day: High rates of algae production will require ample solar insolation. A minimum of 4.65 kWh/m²/day (equivalent to 400 cal/cm²/day) for sustained high growth rates was identified by Benemann, etc. [159]; • Slope $\leq 5\%$: Algae production in open ponds commonly requires land with a slope no greater than 5% cited in US DOE report [160]. Only elevations below 3,000 ft were included in analyses to ensure a year round “frost-free” climate. • Zoning: Algae production is likely to be prohibited in residential areas. Most other zones, however, could possibly allow some algae production. Zones identified as conducive to the production of algae in open ponds in this study include the State Land Use Agricultural and Conservation Districts and county industrial zones. County zones where aquaculture was listed as a permitted land use were also included. • Contiguous area of at least 1,000 acres: Growing algae for biofuels will require a large quantity of algae, and thus a large growing area, e.g. a minimum of 1,000 acres. • Potential nutrient sources: Potential nutrient sources include combustion power plants, landfills, and wastewater treatment plants. 							

3.2 Scale of an Island-based Biorefinery

Three possible value chain models are depicted in Figures 3.2a-c. Figure 3.2a shows a vertically-integrated system for feedstock production and logistics with a conversion facility. Figure 3.2b presents a model of potentially independent growers producing feedstock that is aggregated at a conversion facility. In both Figures 3.2a and 3.2b, all feedstock preprocessing, other than perhaps ambient drying, occurs at the central conversion facility. Figure 3.2c depicts decentralized feedstock production with intermediate aggregation points, preprocessing biomass to higher energy densities for transport to a final conversion facility.

As discussed earlier, appropriate scales for biorefineries in Hawaii will be partly defined by the scale of the feedstock supply. The maximum scale of the processing facility is not only limited by the amount of land available for feedstock production but also by the cost of transporting the feedstock. Generally speaking, the cost for transportation is a function of the specific energy density of a feedstock. High bulk energy densities (e.g. corn, bio-oil, torrefied and pelletized wood) correspond to lower transportation cost and, consequently, allow for a larger size of processing facilities.

Current examples of agricultural production of primary feedstocks (e.g. sugar, fiber, oil, and starch) in Hawaii can serve as benchmarks for this analysis. One of the largest agricultural producers in the State manages ~36,000 acres devoted to a single crop using an approach similar to Figure 3.2a. This scale was selected as a medium benchmark for feedstock production. Based on the data presented in Tables 3.1 and 3.2, two additional scale scenarios of 15,000 and 100,000 acres (smaller and larger, respectively), were considered for biorefineries of terrestrial or aquatic biomass. It is assumed that land has adequate water resources (either through rainfall or irrigation), solar insolation and soil quality for growing any of the considered terrestrial crops or algae.

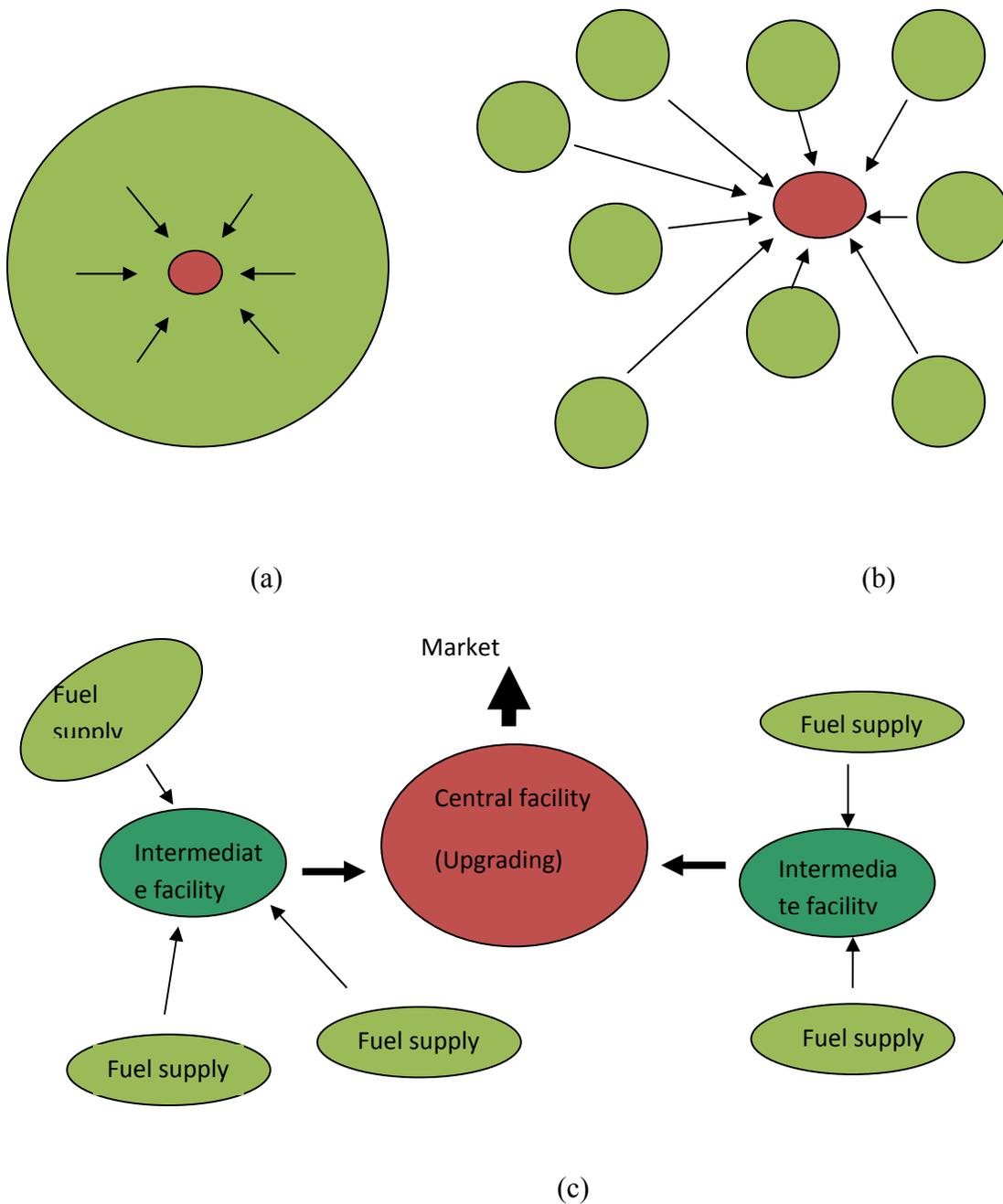


Figure 3.2. Organizational structures for biorefinery supply chains

- (a) Vertically integrated, stand-alone biorefinery with surrounding farm land;*
 - (b) Central biorefinery supplied with feedstock by independent or cooperatively organized growers;*
 - (c) Central biorefinery supplied by intermediate fuel preprocessing facilities;*
- 1. Fuel supply: Biomass is produced, harvested and shipped to an intermediate processing or conversion facility*
 - 2. Intermediate facility: A preprocessing platform (e.g. drying, pyrolysis, torrefaction, pelletization, etc.) to intermediate products*
 - 3. Central facility: Biorefinery for production of final commercial products*

3.3 Matching Platform Technologies with Energy Crops and Scale Scenarios for (Sub) tropical, Island-based Biorefineries

Table 3.3 provides a summary of potential bioenergy/biofuel feedstocks, their typical yield and nutrient and water requirements, and their current agricultural readiness in Hawaii at the three scales identified above.

Table 3.3. Energy crop overview

Feedstock	Typical yield ^a	Primary Product(s)	Nutrient requirements ^b	Total water requirements ^b	Agricultural Readiness in Hawaii?
	[tonne/acre/year]	[-]	[kg N/ha]	[mm]	[-]
Sugarcane	50 ^{c,h}	sugar fiber	100-150 ^m	1,500-1,800 ^m	yes
Corn	8 ^d	starch fiber	157 ⁱ	600 ^j	no
Cassava	20 ^e	starch fiber	100 ^k	1,200-1,500 ^l	no
Banagrass	21.5 ^{e,h}	fiber	100-150 ^m	1,500-1,800 ^m	no
<i>Leuceana</i>	10 ^{f,h}	fiber	0 ^{m,p}	500-1,000 ^{m,p}	no
<i>Eucalyptus</i>	10 ^{g,h}	fiber	0 ^p	> 1,000 ^{m,p}	yes
<i>Jatropha</i>	114 ⁿ gal/acre/year	oil	n.a.	n.a.	no
Algae	1,850 ^o gal/acre/year	oil	n.a.	n.a.	no

Note:

^a per year; ^b per harvested crop; ^c two-year rotation; ^d two harvest per year each averaging 160 bushel/acre; ^e one harvest per year; ^f six-year rotation; ^g seven-year rotation; ^h [10]; ⁱ [11]; ^j [12]; ^k [13]; ^l [14]; ^m [15]; ⁿ[16]; ^o [17]; ^p no irrigation for tree crops, no fertilization beyond initial seedling establishment

Table 3.4 qualitatively summarizes the technological status (lab-, pilot-, demo- and commercial scale), required feedstocks, products, and coproducts for the conversion technologies considered in section 2.

Table 3.4. Qualitative technology overview

	Technology status ¹	Products	Feedstock	Co-products
Ethanol from biochemical route				
Sugar	C	EtOH	sugar	electricity
Starch (corn)	C	EtOH	starch	electricity, DDG
Cellulosic	D	EtOH	fiber	electricity
Gasification				
Heat	C	process heat	fiber	none
Combined Cycle	D/C	electricity	fiber	process heat
IC Engine	D/C	electricity	fiber	process heat
FT-Synfuels	D/C	Syngas, FT-gasoline, FT-diesel	fiber	process heat, electricity
Pyrolysis				
Bio-oil production	D/C	bio-oil	fiber	none
Charcoal production	D/C	charcoal	fiber	none
Bio-oil production for transportation fuels	P/D	Gasoline, diesel, jet-fuel	fiber	none
Combustion	C	electricity	fiber	process heat
Biodiesel via transesterification of veg.oil	C	biodiesel	veg.oil, terrestrial or aquatic origin	oil cake
Renewable diesel via hydrotreating of veg. oil	D	renewable diesel	veg.oil, terrestrial or aquatic origin	none
Anaerobic digestion				
Methane	C	Methane gas	sugars, starches, protein, fats, org. acids, alcohols	nutrient-rich water and digestate (sludge)
Power	C	electricity		
Torrefaction	D	torrefied wood	fiber	none
¹ P = pilot scale, D = demonstration scale, C = commercial scale				

Table 3.5 summarizes conversion technology characteristics (e.g. quantities of products, their energy content, and cost data) when they are matched with various feedstocks based on the three scale scenarios for (sub)tropical, island-based biorefineries. These data should be considered preliminary estimates due to the large number of data sources and the limited ability to normalize information across data sources. Nonetheless, the table provides qualitative, side-by-side comparison of conversion technologies and feedstock options.

Table 3.5. Qualitative technology and crop overview of the output from various platforms based on annual crop yields at three scales scenarios for a biorefinery

Feedstock/ yield/HHV	Biorefinery platform	Key Data	15,000 acres	36,000 acres	100,000 acres
Sugar Cane ^a 50 tonne/acre 4.7 MJ/kg ^b	Biochem. conversion (sugar platform)	Input: feedstock, M tonnes	0.75	1.80	5.00
		Output: EtOH, Mgal. (GWh _{th})	14 (345)	34 (839)	95 (2344)
		Output: electricity, GWh	72	173	480
		Capital cost estimate, \$/gal. capacity ^h	2.7	2.0	1.5
Corn ^c 8 tonne/acre 16.0 MJ/kg	Biochem. conversion (starch platform)	Input: feedstock, M tonnes	0.12	0.28	0.79
		Output: EtOH, Mgal. (GWh _{th})	13 (317)	32 (770)	87 (2,153)
		Output: electricity, GWh	28	69	190
		Capital cost estimate, \$/gal. capacity ^h	1.8	1.2	0.9
Cassava ^d 20 tonne/acre 6.7 MJ/kg	Biochem. conversion (starch platform)	Input: feedstock, M tonnes	0.30	0.72	2.00
		Output: EtOH, Mgal. (GWh _{th})	13 (316)	31 (769)	87 (2149)
		Output: electricity, GWh	17	40	110
		Capital cost estimate, \$/gal. capacity ^h	2.2	1.7	1.2
Banagrass ^e 21.5 tonne/acre 18.0 MJ/kg	Biochem. conversion (lignocellulosic platform)	Input: feedstock, M tonnes	0.32	0.77	2.15
		Output: EtOH, Mgal. (GWh _{th})	25 (614)	61 (1505)	169 (4181)
		Output: electricity, GWh	44	105	292
		Capital cost estimate, \$/gal. cap.	no data	6.9	no data
	Fast-pyrolysis	Output: Bio-oil, M tonnes (GWh _{th}) ^j	0.19 (1037)	0.46 (2490)	1.29 (6916)
		Output: electricity, GWh ^k	0	0	0
		Production cost estimate, \$/t ^l	100-700	100-700	100-700
		Total capital investment, M\$ ^m	30-80	~106	~295
	Gasification ethanol synthesis ^f	Output: EtOH, Mgal. (GWh _{th})	26 (639)	63 (1553)	176 (4339)
		Output: electricity, GWh	0	0	0
		Production cost estimate, \$/gal.	1.72	1.38	1.13
		Total capital investment, M\$	72	134	275
	Gasification FT-synthesis ^g	Output: Gasoline eq., Mgal. (GWh _{th})	15 (645)	37 (1548)	102 (4299)
		Co-output: electricity, GWh	63	152	421
		Production cost estimate, \$/gal.	n.a	4.80	n.a
		Total capital investment, M\$	291	548	1114
Eucalyptus ^e 10 tonne/acre 19.0 MJ/kg	Biochem. conversion (lignocellulosic platform)	Input: feedstock, M tonnes	0.15	0.36	1.00
		Output: EtOH, Mgal. (GWh _{th})	12 (292)	28 (700)	79 (1945)
		Output: electricity, GWh	20	49	136
		Capital cost estimate, \$/gal. capacity	no data	6.9 \$/MGY	no data
	Fast-pyrolysis	Output: Bio-oil, M tonnes (GWh _{th}) ⁿ	0.10 (595)	0.25 (1428)	0.70 (3966)
		Co-output: electricity, GWh ^k	0	0	0
		Production cost estimate, \$/t ^l	100-700	100-700	100-700
		Total capital investment, M\$ ^m	15-38	~50	~140
	Gasification ethanol synthesis ^f	Output: EtOH, Mgal. (GWh _{th})	12 (297)	30 (722)	82 (2018)
		Output: electricity, GWh	0	0	0
		Production cost estimate, \$/gal.	2.46	1.62	1.33
		Total capital investment, M\$	42	80	161
	Gasification FT-synthesis ^g	Output: Gasoline eq., Mgal. (GWh _{th})	7 (300)	17 (720)	47 (1999)
		Output: electricity, GWh	29	71	196
		Production cost estimate, \$/gal.	n.a	n.a	4.80
		Total capital investment, M\$	171	318	648
Leucaena ^e 10 tonne/acre 19.5 MJ/kg	Biochem. conversion (lignocellulosic platform)	Input: feedstock, M tonnes	0.15	0.36	1.00
		Output: EtOH, Mgal. (GWh _{th})	12 (292)	28 (700)	79 (1945)
		Output: electricity, GWh	20	49	136
		Capital cost estimate, \$/gal. capacity	no data	6.9	no data
	Fast-pyrolysis	Output: Bio-oil, M tonnes (GWh _{th}) ^o	0.10 (610)	0.25 (1463)	0.70 (4064)
		Output: electricity, GWh ^k	0	0	0

		Production cost estimate, \$/t ^f	100-700	100-700	100-700
		Total capital investment, M\$ ^m	15-38	~50	~140
	Gasification ethanol synthesis ^f	Output: EtOH, Mgal. (GWh _{th})	12 (297)	30 (722)	82 (2018)
		Output: electricity, GWh	0	0	0
		Production cost estimate, \$/gal.	2.46	1.62	1.33
		Total capital investment, M\$	42	80	161
	Gasification FT-synthesis ^g	Output: Gasoline eq., Mgal. (GWh _{th})	7 (300)	17 (720)	47 (1999)
		Output: electricity, GWh	29	71	196
		Production cost estimate, \$/gal.	n.a	n.a	4.80
		Total capital investment, M\$	171	318	648
Jatropha 114 gal/acre 33 MJ/L	Trans- esterification	Input: feedstock, Mgal.	1.7	4.1	11.4
		Input: thermal, GWh	2.2	5.2	14.5
		Input: electric, GWh	0.1	0.3	0.9
		Output: EtOH, Mgal. (GWh _{th}) ^p	1.7 (59)	4.1 (142)	11.4 (395)
		Capital cost estimate, \$/gal. capacity	2.2	1.5	1.0
Algae 1,852 gal/acre 33 MJ/L	Harvest and Trans- esterification	Input: feedstock, Mgal.	28	67	185
		Input: thermal, GWh	202	485	1348
		Input: electric, GWh ^r	61	146	404
		Output: Biodiesel, Mgal. (GWh _{th}) ^q	28 (963)	67 (2310)	185 (6417)
		Capital cost estimate, \$/gal. capacity	no data	no data	no data

Notes:

In all cases it was assumed that there is no change in the mass conversion or efficiency with scale; only the costs are influenced by scale (when information was available). With the exception of the transesterification platform, all conversion platforms are thermally self-sufficient.

^a based on historic production data in Hawaii, burned and cropped.

^b assuming $HHV_{\text{sucrose}} = 16.5\text{MJ/kg}$ and $HHV_{\text{bagasse}} = 19.2\text{MJ/kg}$ and 13.5% sucrose, 13% fibre.

^c shelled corn, assuming two harvests per year with 160 bushel/acre.

^d fresh tuber weight, 25% starch content.

^e dry, 0 wt% moisture.

^f Ref. [8].

○ Assumed that 1 kg or 1.27 L or 0.33 gal EtOH can be produced from 4.01 kg biomass; or 1 tonne biomass can produced 82 Gal EtOH;

○ €100 million capital cost for the plant with a scale of 1,800 tonne biomass input per day, or 60 million gal EtOH output,

○ Converted to dollars where €1.0 = \$1.3

^g Ref. [7].

○ Conversion of 179 L FT liquids per tonne biomass input, $HHV=152\text{MJ/gal}$ of FT liquid.

○ 707 MJ electricity produced per tonne of dry biomass, converted to 196 MWh.

○ Basic scale: 2,000 t/d biomass input, 32.3 GGE output/year, and \$498 million for capital cost; scale factor: 0.7.

^h Capital investment for anaerobic digestion and CHP is not included. Refer to Table 2.2 for a cost estimate.

- ^j mass conversion of 60% dry basis for grasses [1], energy content was estimated by assuming a fuel-based net efficiency of 65% giving a HHV of 19.3 MJ/kg for dry bio-oil, cf. Table 2.4.2.6. It should be noted that the energy conversion is estimated as no data is available for banagrass.
- ^k electrical output/input is zero as it is assumed that for a fully integrated and optimized commercial scale facility the fuel-gas produced during the process would have sufficient energy to generate the on-site electricity requirements, cf. Section 2.4.2.1.3, sub-section U2.
- ^l production cost data (estimates) vary widely depending on the source (due to the different assumptions and bases used), a ballpark range is \$100-700/t bio-oil output when the feedstock cost is \$0-100 per dry tonne; cf. Section 2.4.2.1.7.
- ^m capital cost data (estimates) are only available for a scale of ~220 t/d dry input (80,000 t/y, year = 365 days) at \$9-20 million, and 1,000 t/d dry input at \$50 million; therefore capital costs are based on multiples of 220 or 1,000 t/d dry input units; cf. Section 2.4.2.1.7.
- ⁿ mass conversion of 70% dry basis for woody biomass, energy content was estimated by assuming a fuel-based net efficiency of 75% giving a HHV of 20.4 MJ/kg for dry bio-oil, cf. Table 2.4.2.6.
- ^o mass conversion of 70% dry basis for woody biomass, energy content was estimated by assuming a fuel-based net efficiency of 75% giving a HHV of 20.9 MJ/kg for dry bio-oil, cf. Table 2.4.2.6.
- ^p based on 114 gallons per year per acre.
- ^q based on 1850 gallons per year per acre.
- ^r includes electrical needs for harvest, drying, extraction and transesterification (based on Xu et al. [9]).

3.3.1 Biorefinery Based on Biochemical Platform

With the exception of conversions involving sugars derived from lignocellulosic feedstocks, the investigated biochemical platforms are well established and yield, cost and conversion efficiency data are readily available. However, assumptions and projections were made to accommodate the integration of an anaerobic digester into each biochemical platform technology. The combustion of biogas to generate process heat and electricity allows the starch platform technology to become thermally self-sufficient and to generate excess electricity that can be fed into the grid. The lignocellulosic- and sugar platform do not rely on biogas combustion to be thermally self-sufficient. However, their output of excess electricity is enhanced by integrating anaerobic digestion into the conversion process. Consequently, all investigated biochemical platforms are thermally autonomous and, moreover, produce an excess amount of electricity.

On a 36,000 acre basis, the biochemical conversion of banagrass to ethanol yields the largest annual amount of ethanol (61 MGY) followed by sugar cane (34 MGY), corn (32 MGY) and cassava (31 MGY). The lignocellulosic tree crops *Eucalyptus* and *Leucaena* both yield about 12 MGY due to their lower annual productivity. The largest amount of annual surplus electricity is generated by the sugar cane process (173 GWh) trailed by banagrass (105 GWh), corn (69 GWh) and cassava (40 GWh). Again, the tree crops *Eucalyptus* and *Leucaena* yield less surplus electricity (20 GWh). The investment cost projections for the biochemical technologies on a 36,000 acre basis show the lowest capital requirements for a corn to ethanol facility (1.2 M\$/MGY), followed by cassava (1.7 M\$/MGY), sugar cane (2 M\$/MGY) and lignocellulosic biomass (6.9 M\$/MGY). Only the corn to ethanol process offers the possibility to produce a valuable co-product in the form of Dried Distillers Grain (DDG). The availability of locally produced DDG in the State has the potential to supply a range of animal feeding operations and thus to increase the production of locally produced meat products.

In the case of corn and cassava, non-starchy biomass leftover from the harvest (i.e. corn stover and above ground cassava biomass) could potentially be used to generate further electricity through combustion. Alternatively, the biomass could be used to augment the soil after composting. Other processing technologies such as pyrolysis or gasification are imaginable assuming that the processing capacities are already existent and in close proximity.

Compared to thermal conversion technologies, biochemical conversions are characterized by high technological readiness paired with comparatively low capital requirements and average energetic conversion efficiencies. One of the main drawbacks of biochemically produced ethanol can be found in ethanol's limited versatility. Although ethanol can be used to partially or fully replace gasoline, it cannot substitute for diesel or jet fuel. However, new biochemical conversion technologies are starting to advance from the lab-scale to pilot- and demonstration scale (see Table 2.12). Often, these technologies are proprietary in nature and exploit a variety of microorganism and pathways to convert sugars to more versatile products such as vegetable oil, higher molecular weight alcohols and organic acids. Known problematic areas of biochemical conversions include cane-trash burning for sugar cane farming and the production of a low-value neutralizing salt during lignocellulosic ethanol production. Furthermore, the large-scale farming of energy crops such as sugar cane, corn, cassava and banagrass requires large amounts of fertilizer and water. Long term effects on soil quality and surrounding ecosystems have not been studied with the exception of sugar cane.

3.3.2 Biorefinery Based on Chemical Platform

The transesterification of vegetable oils to biodiesel is a process that is well understood and has been commercially adapted throughout the world. Although the technology offers high conversion efficiency, low yields of oil bearing crops are a limitation. *Jatropha*, the only terrestrial oil crop investigated in this report, yields about 114 gal/acre/year of biodiesel or 4.1 MGY on a 36,000 acre basis [50]. Although there is a general lack of large scale production data for algae and systems for fuel production are currently unproven [34], current estimates suggest that 67 MGY of vegetable oil could be produced on 36,000 acre of land. Capital cost requirements, pond contamination, oil harvest and purification still represent large economic and technological hurdles.

3.3.3 Biorefinery Based on the Torrefaction and Pyrolysis Platforms

Torrefaction

Torrefaction of biomass to produce torrefied wood is a relatively new technology when compared to other thermochemical processes discussed in this report. Torrefied wood is a solid fuel which is similar to coal or char in many aspects. Its main benefits include low stable moisture content, increased caloric value, improved grindability and high process efficiency. Torrefied wood can be further processed by pelletization to take advantage of improved grinding properties (TOP process) when compared to biomass. The resulting TOP pellets have about two thirds of the bulk energy of coal and are easier to transport and store than biomass and torrefied (unpelletized) biomass [58, 65, 66]. This approach is widely considered to be the mostly likely scenario for a commercial torrefaction facility (see Section 2.4.1 for further details).

Torrefied wood has been shown suitable for co-firing applications with coal, oil and natural gas for electricity generation. However, caution is warranted as only limited tests have been performed and the upper limits for co-firing have not been established. Torrefied biomass could also be used as a fuel for gasification processes for electricity generation, and possibly for FT-synthesis to produce replacement transportation fuels or chemicals. However, limited information is available regarding gasification systems using torrefied biomass as a fuel supply.

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 reactor configuration and reaction conditions. 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 [1]. Nonetheless, a number of companies are now offering 'off-the-shelf' fast-pyrolysis units at scales up to 400 t/d dry input [2]. However, due to a lack of operational commercial facilities and the proprietary nature of cost and efficiency data, limited information is available (see Section 2.4.2.1 for details).

As a means of comparing fast-pyrolysis to other technologies outlined in Table 3.4, the following assumptions were used: dry biomass is converted to bio-oil with a mass conversion of 70% for woody biomass and 60% for grasses [1]; the fuel based process efficiency (defined in Section 2.4.2.1.1) is 75% for woody biomass [1, 2] and 65% for grasses (assumed) on a HHV_{dry} basis; the char produced during the process is sufficient to provide all the thermal requirements of the plant [1, 2]; the fuel-gas produced during the process is sufficient to provide all the electricity requirements of the plant [2]; bio-oil is the only exportable product from the process and upgrading to transportation fuels is *not* considered. The above assumptions are broadly in line with current estimates for a commercial process, although there are variations depending on the specific process considered (see section 2.4.2.1.3 for further details).

Considering a land area of 36,000 acres for supplying biomass to a fast-pyrolysis reactor (Table 3.4), the greatest mass yield of bio-oil can be attributed to banagrass (460,000 tonnes, $\sim 2,500 \text{ GWh}_{\text{th}}$), followed by the tree crops *Leucaena* and *Eucalyptus* with 250,000 tonnes and a corresponding energy content of 1,400 and 1,500 GWh_{th} , respectively. The capital cost of a fast-pyrolysis reactor operating at this scale is on the order of \$100 million and the production cost is in the range of \$100-700 per tonne of bio-oil using recent and current estimates [1, 3-6] (see Section 2.4.2.1.7 for further details).

Bio-oil from fast-pyrolysis may be suitable as a direct replacement for LSFO and coal in existing power stations after relatively minor upgrading steps (e.g. filtration or blending) [1]. For use in stationary diesel engines, the bio-oil would probably require more extensive upgrading and the use of additives which may not prove to be cost effective at present [1, 5]. Bio-oil also has the potential to be upgraded by hydro-treatment or other catalytic processes to produce replacement transportation fuels (gasoline, diesel and jet-fuel). However, these methods have yet to be demonstrated at commercial scale or proven to be financially viable [1]. Refer to Section 2.4.2.1.4 for details regarding upgrading of bio-oils to transportation fuels and to Section 2.4.2.1.5 for potential direct applications for bio-oils. For details on pyrolysis for char production refer to section 2.4.2.2.

3.3.4 Biorefinery Based on the Gasification Platform

A biorefinery based on the gasification platform can produce transportation fuels, bio-ethanol, electricity, SNG, hydrogen and other chemical products such as fertilizers, wax, etc. Generally, any types of crops, agriculture waste, forest waste, and municipal solid waste (MSW) as well as solid residues generated from biochemical/chemical processes, such as fermentation residue, bagasse, etc., can be converted with this platform. Figure 3.6 provides an overview of a biorefinery based on the gasification platform.

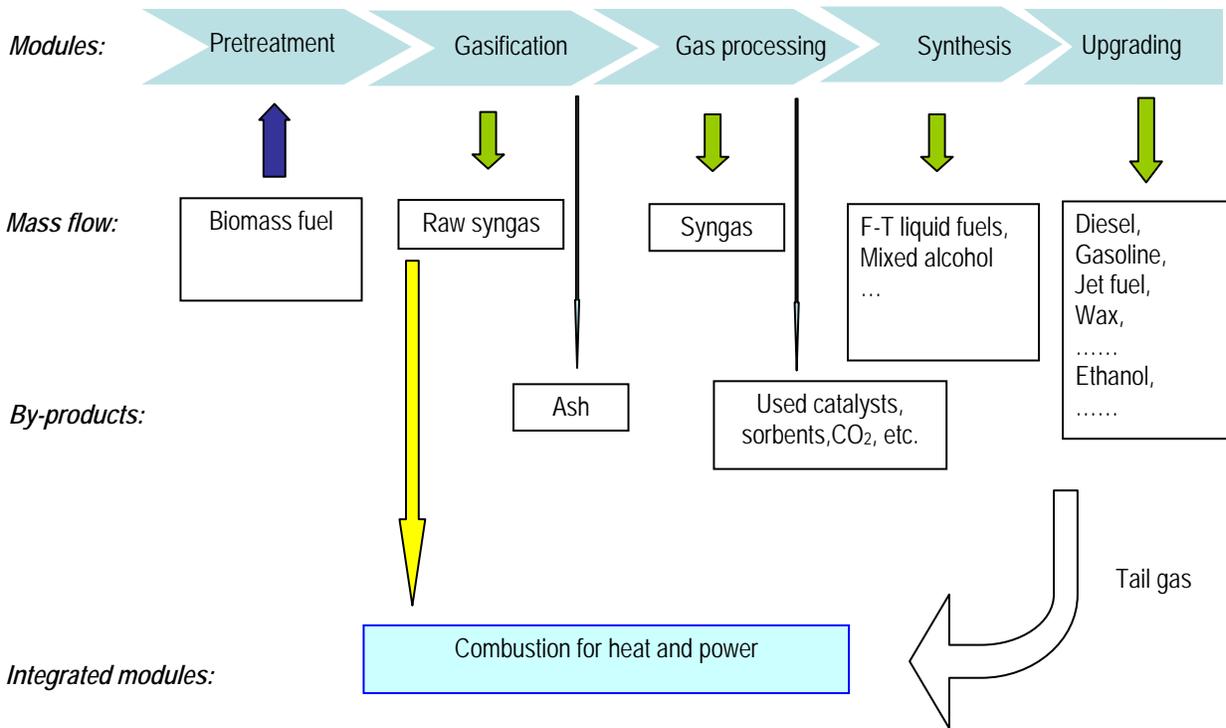


Figure 3.3. Diagram of a biorefinery based on the gasification platform

Banagrass, the lignocellulosic energy crop with the largest yield, produces about 774,000 tonnes of dry matter annually on a 36,000 acre plot (~2,000 tonnes per day). This is enough feedstock to supply a gasification plant with approximately 400 MW thermal input. The crop yields of *Leucaena* and *Eucalyptus* are about 50% of banagrass and, consequently, lend themselves only

to facilities proportionally smaller. Depending on the desired output, two scenarios present themselves (based on 400 MW_{th} input, banagrass):

1. FT synthesis: Based on Swanson's analysis for a LT (low temperature) scenario [7], about 37 MGY of gasoline equivalent and 152 GWh electricity can be produced annually. This would replace about 10 % of Hawaii's motor gasoline consumption and 1.5% of the State's electricity consumption (refer to Figures 3.4 and 3.5). The investment cost of a plant of this scale is estimated to be about \$500 million and the fuel production cost estimates are ~\$4.80 per gallon of gasoline equivalent [7].
2. Ethanol synthesis: He et al. [8] projects an annual output of approximately 63 MGY of ethanol after syngas-to-ethanol conversion. The estimated capital and fuel cost (based on 2011) are \$130 million and \$1.38 per gallon, respectively. No net-output of electricity is projected and the plant is thermally self-sufficient.

Larger scale scenarios (>1,000 MW_{th} input), as projected with the 100,000 acre scenario, are anticipated to require feedstock densification in intermediate facilities (e.g. through torrefaction, pelletization or pyrolysis) prior to gasification to reduce transportation cost and improve storage and handling properties. At this time, small-scale scenarios involving gasification and fuel synthesis (e.g. banagrass on 15,000 acres, or about 170 MW_{th} input) appear economically unfavorable.

4. Conclusion

This report assessed the current state of biorefinery component technologies, their baseline material and energy balances for well-defined feedstock and/or conversion modules and provides preliminary estimation for production costs for the primary product. Based on three scale scenarios for a biorefinery supplied by 15,000, 36,000 and 100,000 acres of adequate agricultural land, the following conclusions could be drawn:

- The medium scale scenario (36,000 acres biomass supply) is considered the most viable in the near future. At this scale, both biochemical and thermochemical based biorefineries could realize economies of scale. The smaller scale (15,000 acre) scenario would be suitable for fewer feedstock-technology options, e.g. banagrass as boiler fuel. The large scale scenario may require development of intermediate processing facilities to increase fuel density and decrease transportation cost. These additional system complexities may be more approachable in the longer term.
- In general, the biochemical conversion technology platforms with the highest level of technological readiness are limited to the production of ethanol, a fuel with relatively low versatility. Thermochemical conversions can provide a more versatile range of fuels (e.g. fuel oil, diesel, gasoline and jet fuel) but generally exhibit a lower technological readiness and often require a larger plant size to be economically viable.
- Thermochemical conversion facilities can process a wide range of feedstock, including agricultural, forest and municipal wastes as well as purpose grown fiber crops. Conversely, biochemical processing plants are usually very specific in feedstock requirements and may rely heavily on large-scale monocultures.
- Energy-dense bio-oil from fast pyrolysis or torrefied-biomass pellets have the potential for direct use in existing power stations to replace/supplement low sulfur fuel oil (LSFO) and/or coal in the short term.

In addition to the previously discussed platform technologies, novel and emerging conversion techniques should not be excluded. Examples include algae farming, syngas fermentations, butanol fermentations, advanced pyrolysis, hydrotreating of plant oils or bio-oil, and advanced

lignocellulosic fermentations. However, due to the proprietary nature of these processes, there is a general lack of data and detailed process descriptions for evaluations. Nonetheless, some of the novel pathway technologies may be a good fit for Hawaii, given its unique circumstances of being an island state with tropical climate, limited amount of farmland, and proportionally large demand for jet fuel and low sulfur fuel oil. Government policies and incentives coupled with market forces and entrepreneurial spirit will ultimately shape the development of biorefineries in Hawaii.

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