Biofuels

Current and Future Processes

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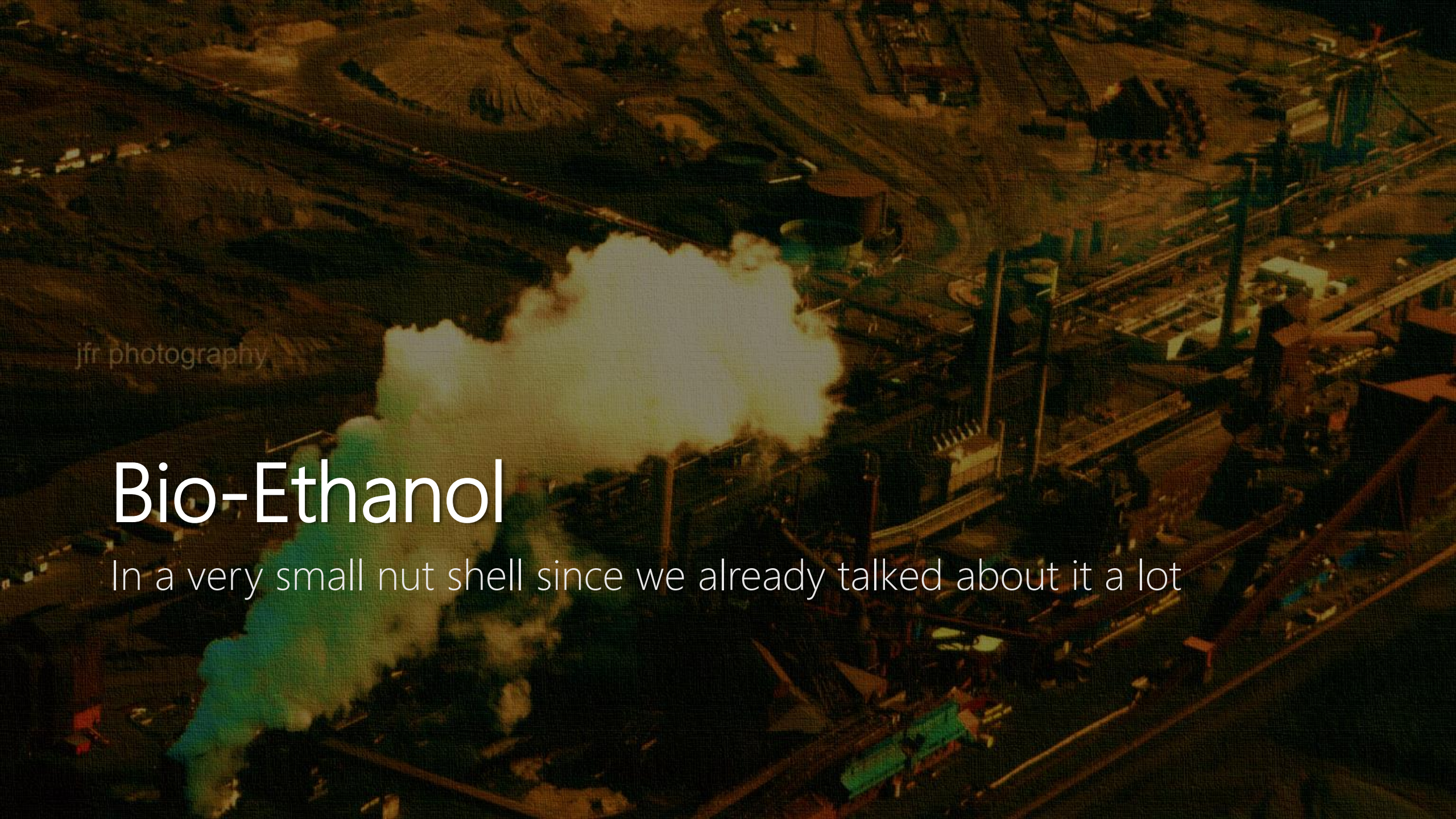
Lecture 5.2 – 2018 Edition

Image: Wikipedia

1st vs 2nd Generation Biofuels

- 1st Generation Biofuels:
  - Fermentation of food
  - Corn
  - Wheat
  - Sugarcane
  - Vegetable Oils
  - Food Starch

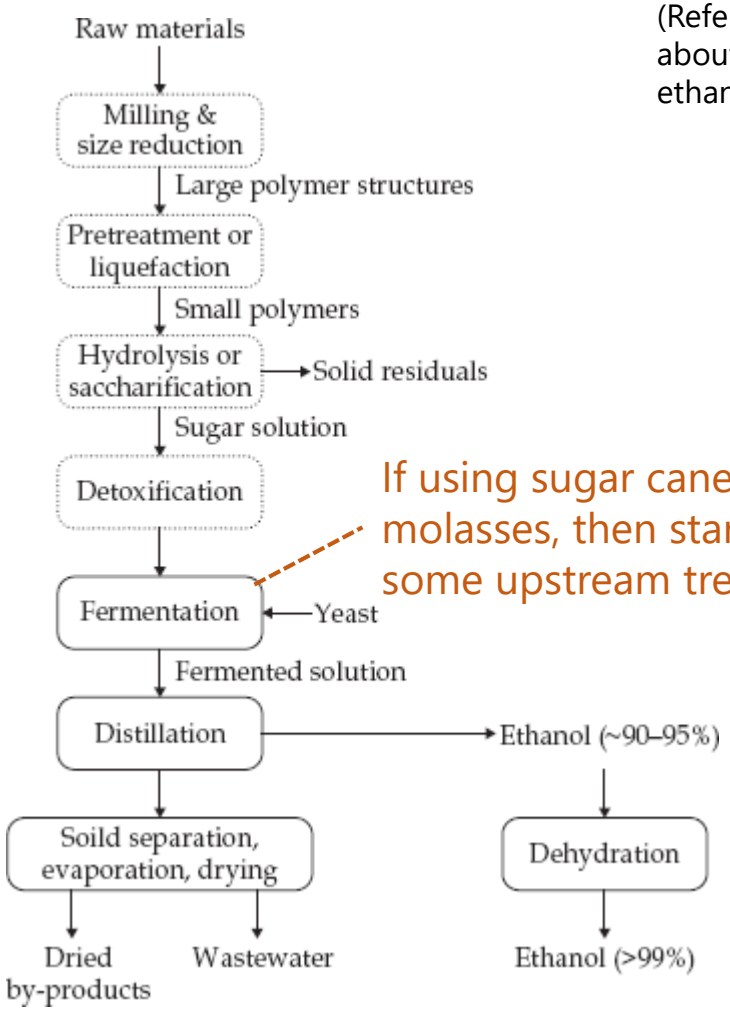
- 2nd Generation Biofuels
  - Non-food sources
  - Switchgrass
  - Seaweed
  - Wood
  - Lignocellulosic biomass
  - Wastes
- The goal is to avoid food competition.
- Potentially could be better on its own anyway.



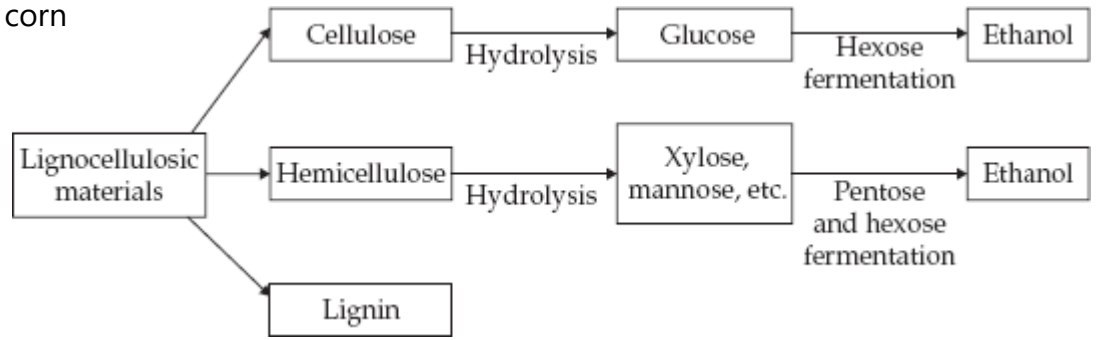
Bio-Ethanol

In a very small nut shell since we already talked about it a lot

Ethanol Production Basics



(Refer to lecture on biofuels for more about the general context of corn ethanol)



If using sugar cane juice or molasses, then start here but with some upstream treatment

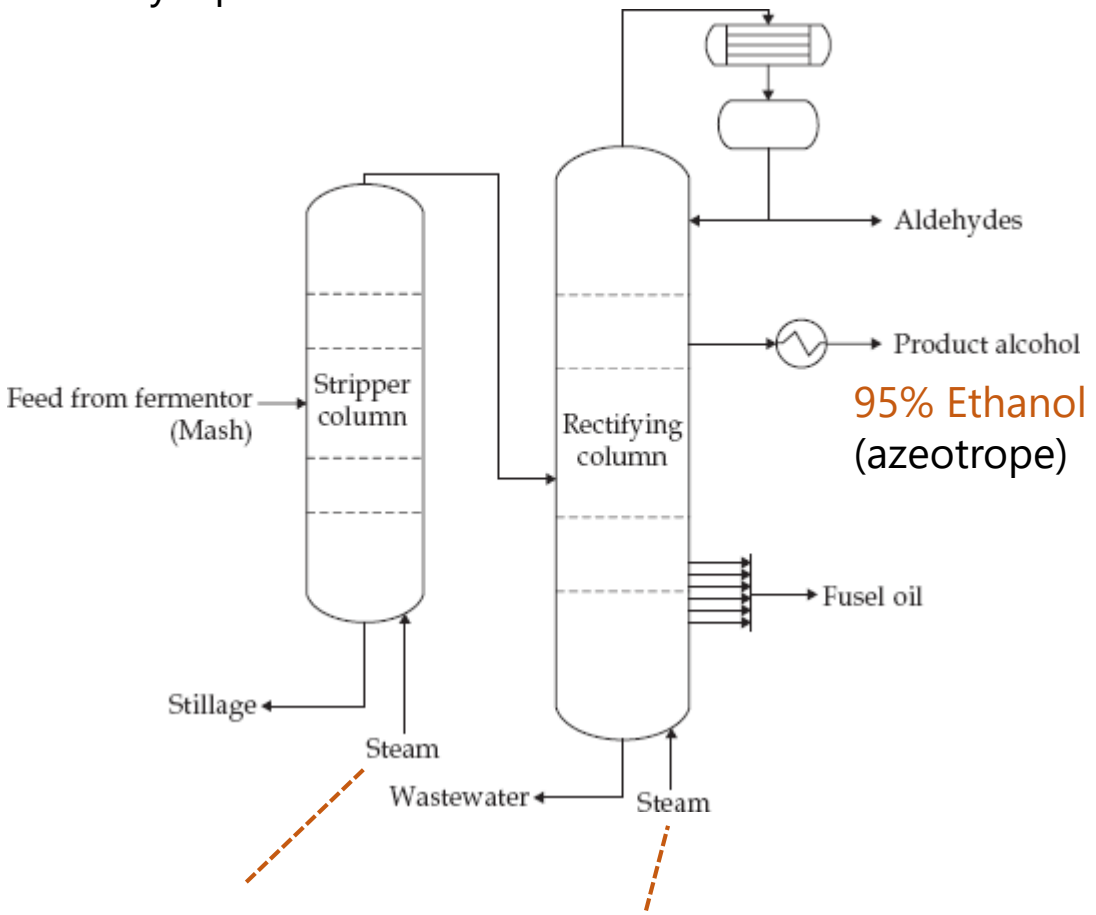
$$C_6H_{12}O_6 \text{ (Hexoses)} \xrightarrow{\text{Microorganisms}} 2C_2H_5OH \text{ (ethanol)} + 2CO_2$$

1/3 of the carbon in the sugar released back as CO_2 before you get to use it as a fuel!

Sources: Nag A. Biofuels Refining and Performance. (2008) McGraw-Hill.

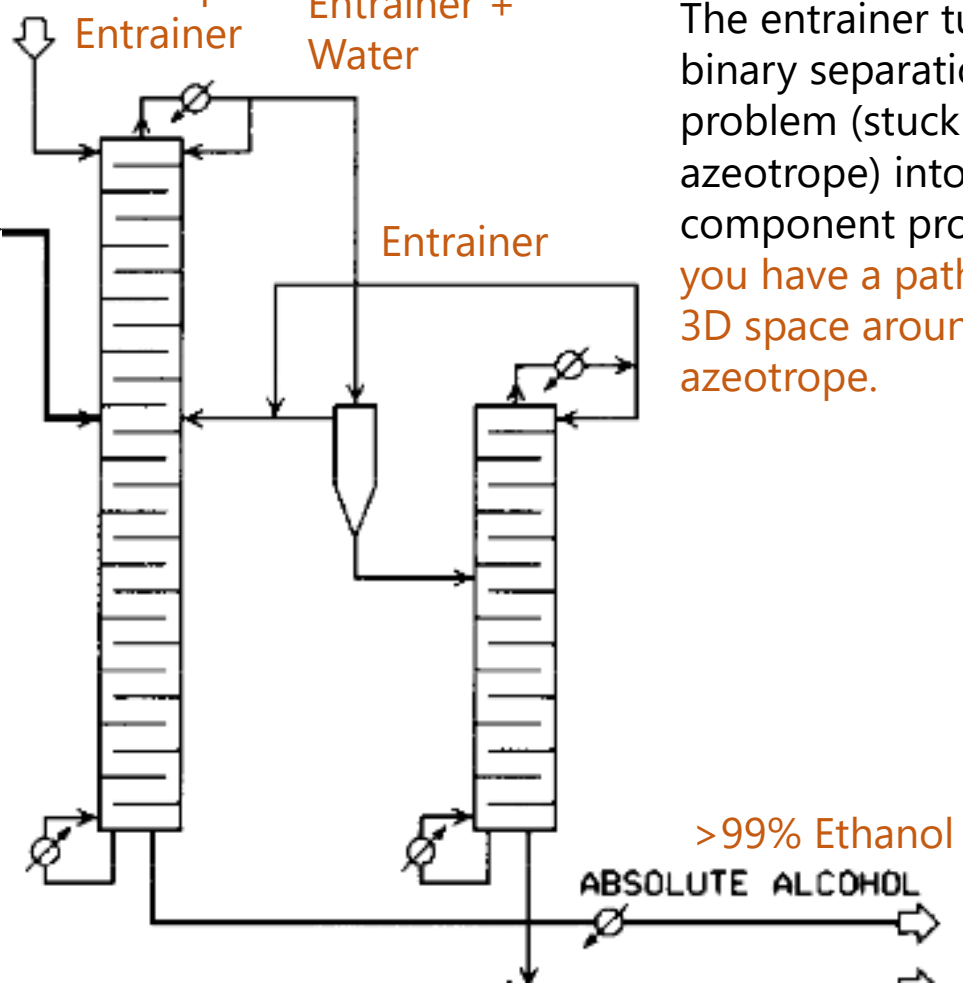
Ethanol Recovery

One of Many Options



95% Ethanol (azeotrope)

Consumes a lot of water & steam here



>99% Ethanol

The entrainer turns the binary separation problem (stuck at azeotrope) into three component problem. So you have a pathway in 3D space around the azeotrope.

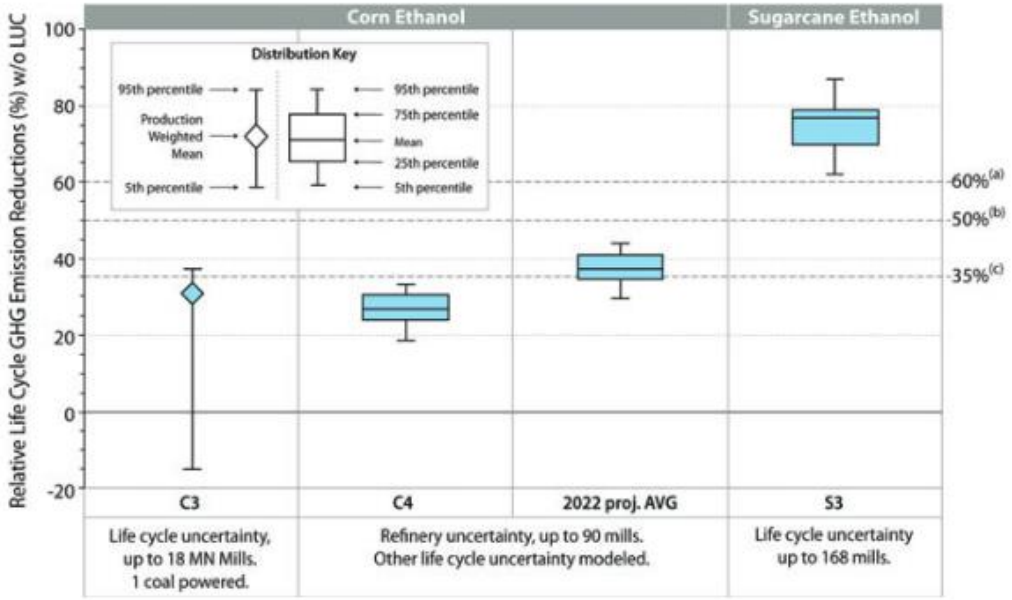
Sources: Nag A. Biofuels Refining and Performance. (2008) McGraw-Hill.
Sander U, Soukup P. Journal of Membrane Science, 36 (1988) 463-475

Production (Worldwide)

County	Amnt. Produced in 2017 (Gallons)	% of World Share
USA (corn)	15.8 Billion	58%
Brazil (sugar)	7.1 Billion	26%
European Union	1.4 Billion	5%
China	0.8 Billion	3%
Canada	0.5 Billion	2%

USA Corn Ethanol	Brazillian Sugarcane Ethanol
9.6% of gasoline	41% of gasoline
20% of all arable land	9% of all arable land
Find little value in displacing gasoline for GHG purposes. Benefit comes from burning the corn wastes to displace electricity.	Double the emissions reductions compared to corn in the more optimistic cases.

These numbers all get worse once you factor in land use chage



Sources: Renewable Fuels Association. World Fuel Ethanol Production. https://ethanolrfa.org/resources/industry/statistics/#1537559649968-e206480c-7160 (2017)
Chum HL, Warner E, Seabra JEA, Macedo IC. A comparison of commercial ethanol production systems from Brazilian sugarcane and US corn. Biofuels Bioproducts & Biorefining. 8:205-223 (2014).

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Bio-Diesel

Bio-Diesel : Recommended by Diesel Himself

- Early 1900s: Rudolf Diesel (inventor of the diesel engine) predicts bio-diesel will become as important as petroleum fuels
  - Many kinds of oils can be used (see right)
  - Not enough land to cover our needs
  - Many kinds of fatty acids and esters will work
  - Some alcohols reacted into esters

Oil source	Production (gal/acre/yr)	Percent of U.S. cropping area*
Microalgae	6280	2
Chinese Tallow tree	700	20
Palm oil	635	22
Coconut oil	287	50
Jatropha	202	71
Castor oil	151	95
Olive oil	129	111
Rapeseed oil	127	112
Corn oil	18	794

This is the % needed to replace current diesel combustion

Triacylglycerol *Alcohol* *Catalyst* *Fatty Acid Ester* *Glycerol*

$$TAG + 3R'OH \longleftrightarrow 3R'COOR + C_3H_5(OH)_3$$

FFA *Acid Catalyst* *Alkyl Ester*

$$RCOOH + R'OH \longleftrightarrow RCOOR' + H_2O$$

Triacylglycerol *Ethyl Acetate* *Lipase* *Ethyl Ester* *Triacetin*

$$TAG + 3CH_2CH_3(OC(O)CH_3) \leftrightarrow 3RCOOCH_2CH_3 + C_3H_5(OC(O)CH_3)_3$$

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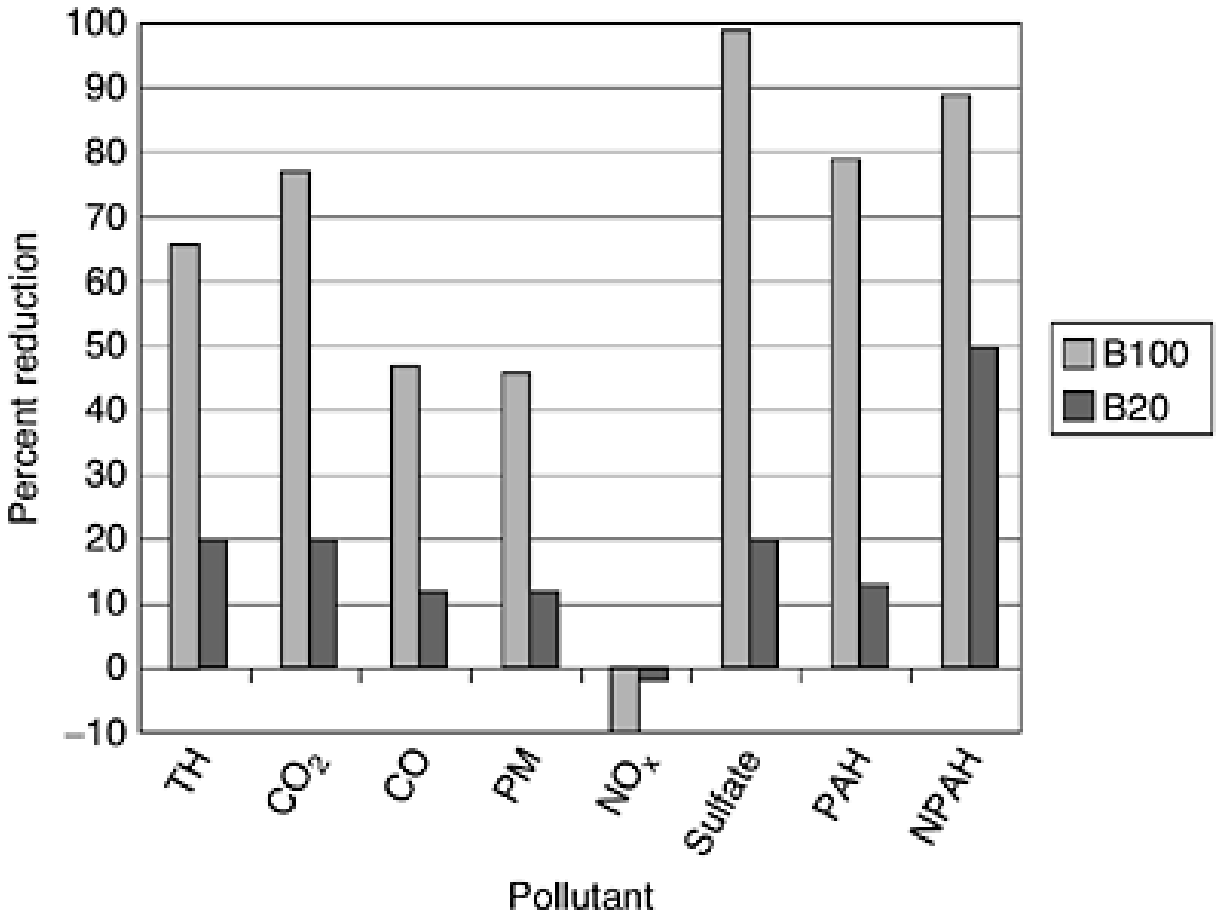
Sources: Drapcho CM, Nghim NP, Walkter T. Biofuels Engineering Process Technology. McGraw Hill (2008)

Emissions Reductions

- Biodiesel has significantly lower lifecycle emissions than petro-diesel in most categories
  - Except NOx, that's a little worse
  - CO_2 reduction here is likely grossly overstated but I can't prove that.



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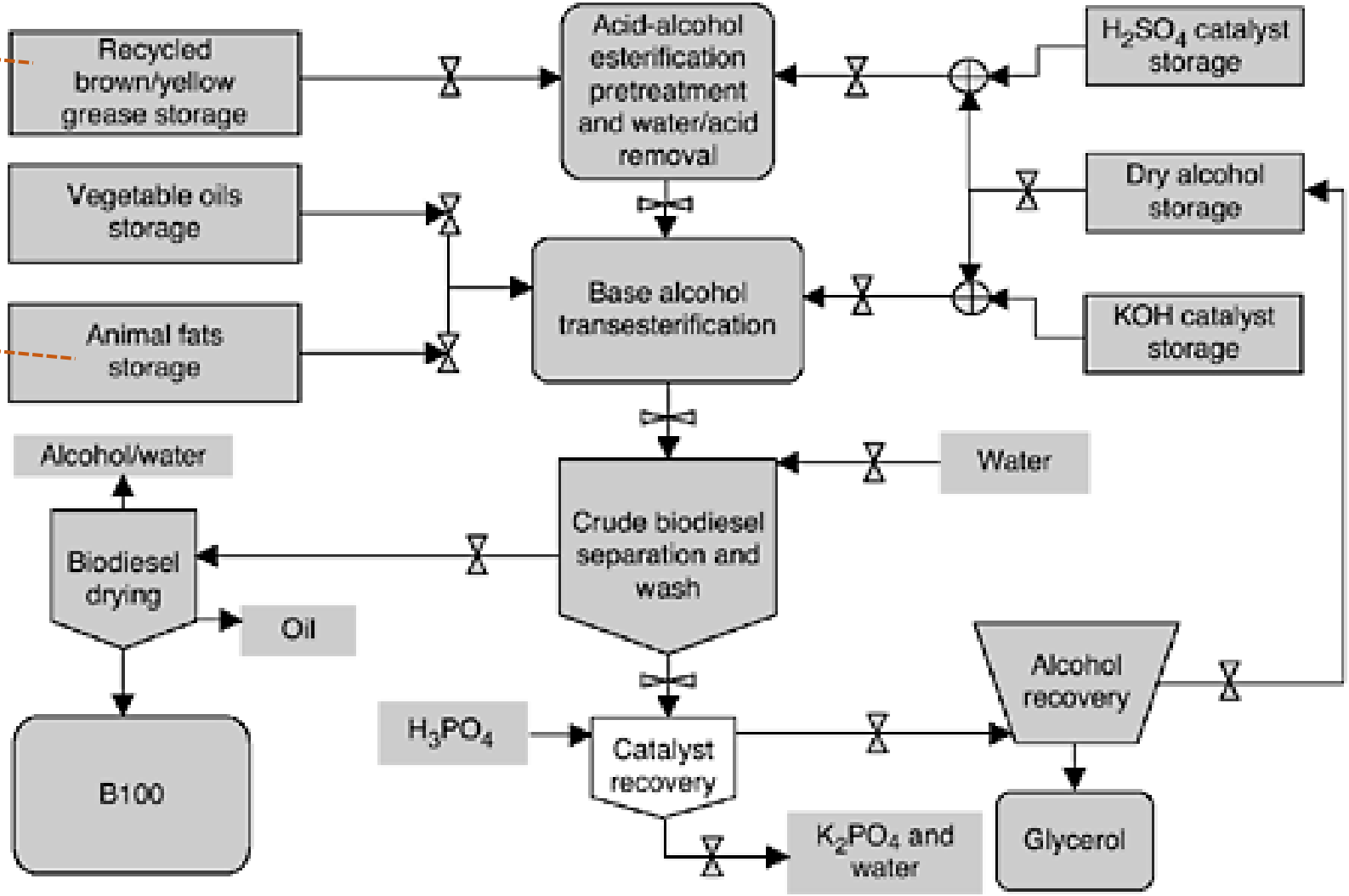
Generic Process



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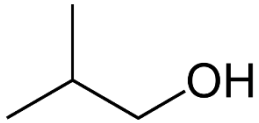
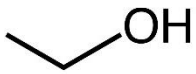
Bio-Butanol

Better than bio-ethanol?

Comparison With Fermentation based Ethanol





	i-Butanol via Fermentation	Ethanol via Fermentation	Gasoline
EROEI	1.4-1.5	1.5	18
Energy Density [MJ/L]	27-29	19.6	32
Miscibility in Gasoline	High	Low	NA
Water Solubility	9.1%	100%	<0.01%
R+M/2 Octane	87	113	86-95
ΔH_{vap} [MJ/kg]	0.43	0.92	0.36
Lifecycle GHG emiss. ($kgCO_2$/gallon of gasoline equiv.)	7.0	6.5	11.25

About half or less?

Sources: Wiebe M, Adams TA II. Assessment of feasibility and benefits of replacing bioethanol with biobutanol in the transportation fuels industry. (2018). LAPSE:2018.0853
Dalle Ave G, Adams TA II. Techno-economic comparison of Acetone-Butanol-Ethanol fermentation using various extractants. Energy Conversion and Management 156 (2018) 288–300

Fermentation Route Same impact as bio-ethanol

Higher energy density than bio-ethanol

Able to mix much more butanol into gasoline than ethanol

Low water solubility means (1) we can pipeline butanol (2) we can mix butanol into the gasoline at the refinery and not at the "last mile"

Not an octane enhancer but at least on-par with conventional 87 gasoline

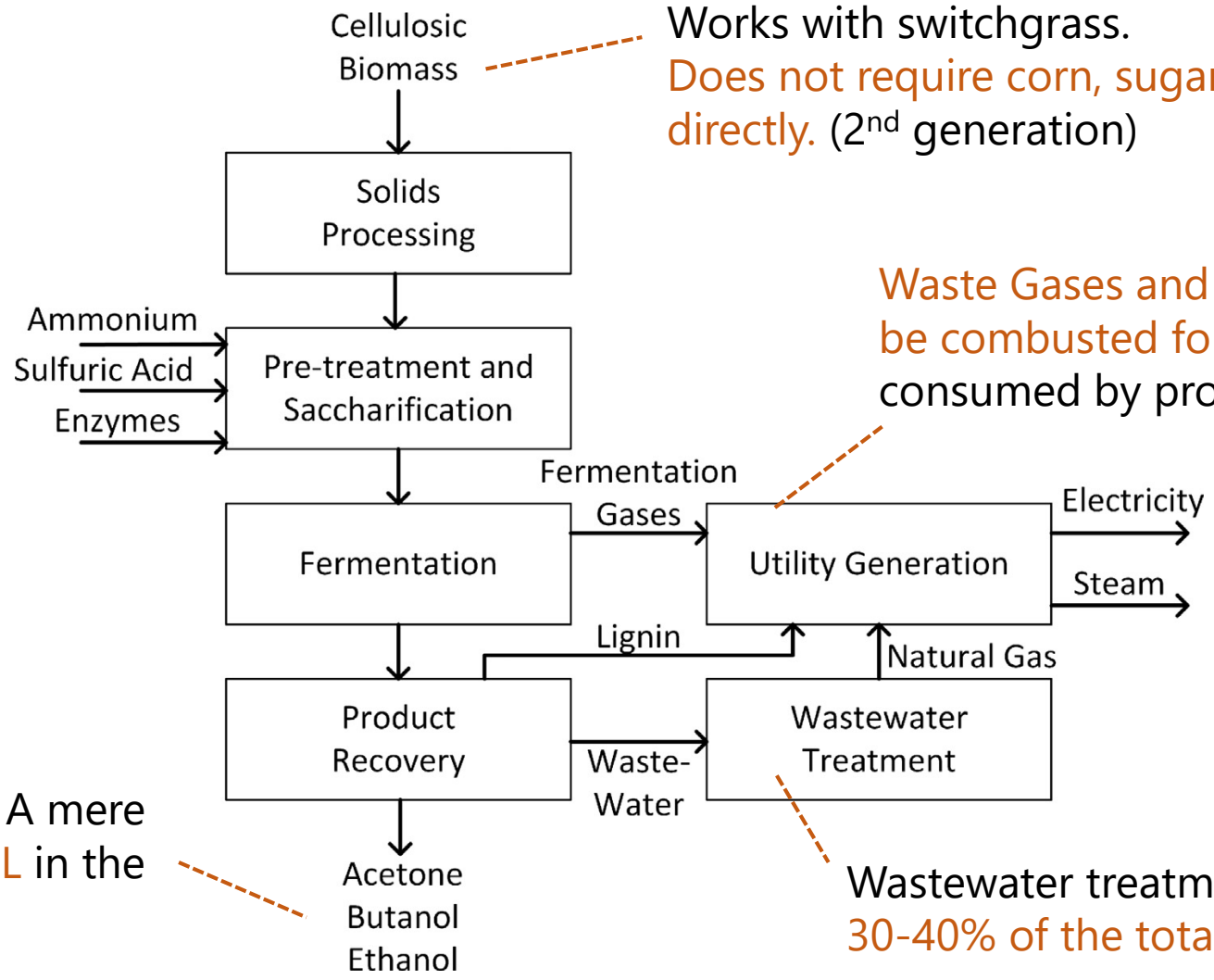
Lower heat of vapourization means much easier to cold-start in winter

Fermentation based Bio-Butanol (ABE Process)

Works with switchgrass.
Does not require corn, sugar directly. (2nd generation)

Need enzymes to convert to sugars

Waste Gases and Non-fermentable Lignin can be combusted for heat and power (more than consumed by process)



We want the butanol. A mere 13 to 35 g of butanol L in the best cases!

Wastewater treatment is massive.
30-40% of the total capital cost!

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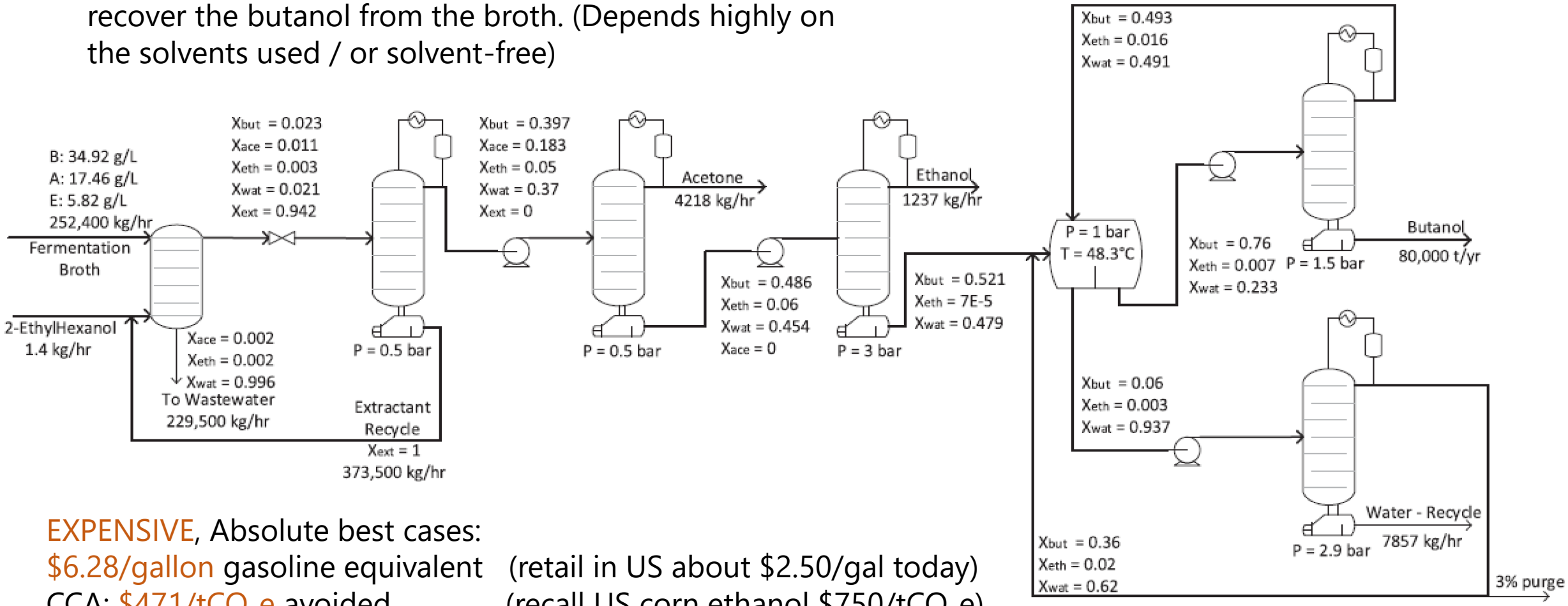
Sources: Dalle Ave G, Adams TA II. Techno-economic comparison of Acetone-Butanol-Ethanol fermentation using various extractants. Energy Conversion and Management 156 (2018) 288–300

Recovery of Butanol from ABE Broth

An example of an optimal distillation process required to recover the butanol from the broth. (Depends highly on the solvents used / or solvent-free)



EXPENSIVE, Absolute best cases:
$6.28/gallon gasoline equivalent (retail in US about $2.50/gal today)
CCA: $471/t$CO_2$e avoided (recall US corn ethanol $750/t$CO_2$e)

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Thermochemical Biobutanol

Wood. Switchgrass. Seaweed!

Solids handling a challenge

Mixed Alcohol Synthesis

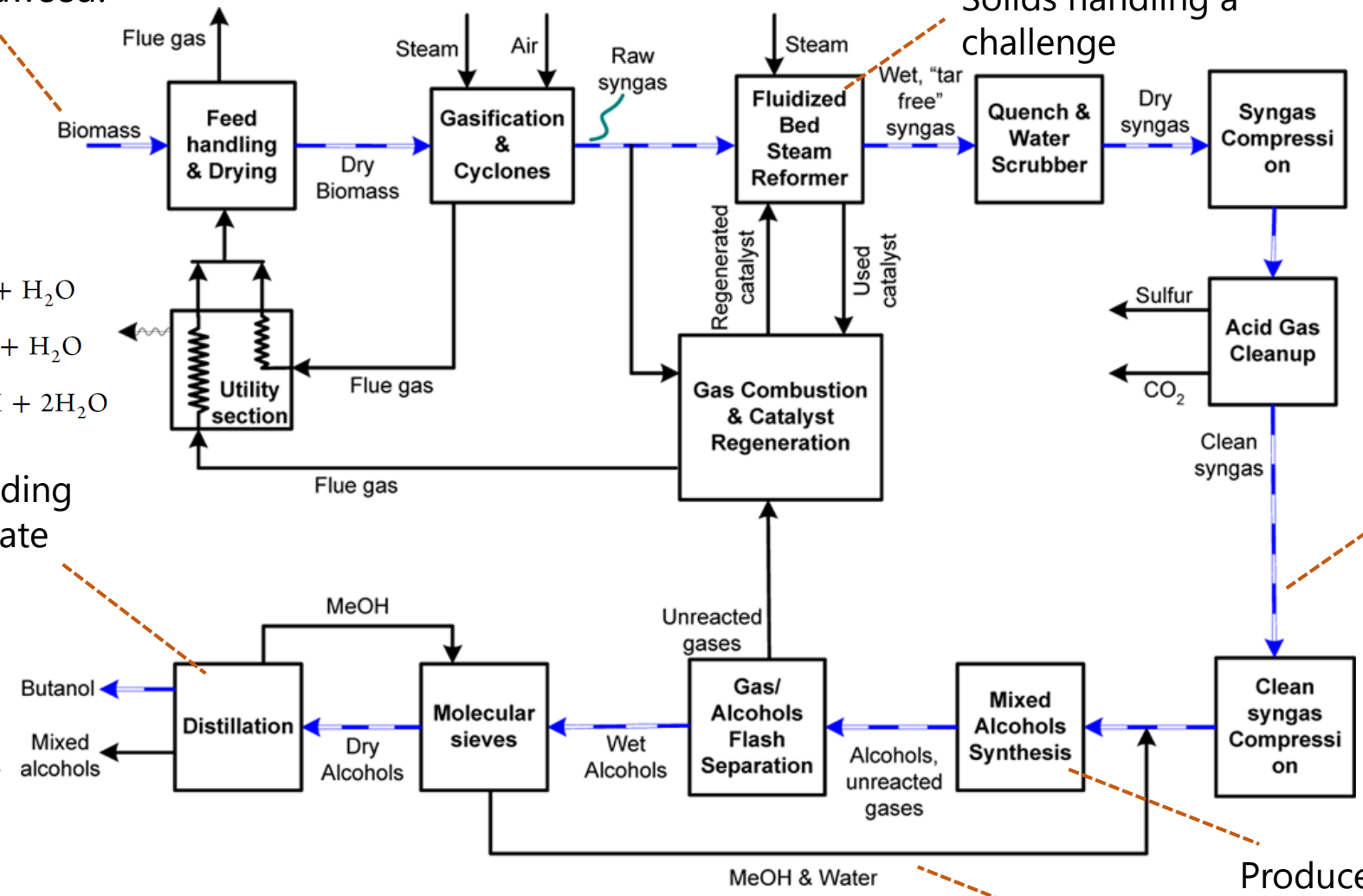
$CO + 2H_2 \leftrightarrow CH_3OH$

$2CH_3OH \rightarrow C_2H_5OH + H_2O$

$CH_3OH + C_2H_5OH \rightarrow C_3H_7OH + H_2O$

$CH_3OH + C_3H_7OH \rightarrow iC_4H_9OH + H_2O$

$2CH_3OH + C_3H_7OH \rightarrow C_5H_{11}OH + 2H_2O$



Classic or advanced (dividing wall) distillation to separate

Now we have clean syngas (H_2 + CO)

Higher (non-fuel) alcohols sold as co-product

Lower alcohols recycled to be re-reacted

Produces mixture of alcohols from methanol to pentanol and a little higher

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Sources: Okoli C, Adams TA II. Ind. Eng. Chem. Res. 2017, 56, 1543–1558
Okoli C, Adams TA II, Brigljevic B, Liu JJ. Energy Convers Manage 123:410-422 (2016).

Economics more promising, but not proven yet

- CCA (theoretical studies):
  - Corn Ethanol: $750/t$CO_2$e (US Congressional Budget Office)
  - Seaweed-to-Butanol via Gasification: $616/t$CO_2$e (in South Korea)
  - Switchgrass-to-Butanol via Fermentation: $471/t$CO_2$e (best known)
  - Wood-to-Butanol via Gasification: $132/t$CO_2$e (best known)
- Maturity wise:
  - Butamax: First major venture into biobutanol. ABE route (will sell the ethanol too)
    - Joint venture between BP and Dupont, has been in the works for a decane
  - Corn ethanol the most mature commercially & widely used in north America
  - Brazilian sugar cane ethanol also quite mature

Sources: Okoli C, Adams TA II. Ind. Eng. Chem. Res. 2017, 56, 1543–1558
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Dalle Ave G, Adams TA II. Techno-economic comparison of Acetone-Butanol-Ethanol fermentation using various extractants. Energy Conversion and Management 156 (2018) 288–300.
Butamax.com