

Bioethanol

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Significance

- Bioethanol is an important biofuel contributing to ~65% of the global biofuel production (BP, 2016).
- Bioethanol is blended to petroleum-derived petrol.
- Bioethanol can offer energy and economic security of developing nations, if produced locally from indigenous biomass (bio-based waste resource).
- Brazil contributes to 25% of the global production (US DOE, 2016).
- Anhydrous bioethanol or E100, and bioethanol by 85% by energy or E85 are used in neat ethanol and flexible-fuel vehicles.
- Bioethanol as liquid transport fuel can help in low-carbon transitioning to net zero carbon future, wherein the transport sector would primarily employ renewable electricity as a source of energy.

Sadhukhan, J., Martinez-Hernandez, E., Amezcua-Allieri, M.A. and Aburto, J., 2019. Economic and environmental impact evaluation of various biomass feedstock for bioethanol production and correlations to lignocellulosic composition. *Bioresource Technology Reports*, 7, p.100230.
<https://doi.org/10.1016/j.biteb.2019.100230>

Sustainability

- Bioethanol produced from the first generation feedstock, corn, sugarcane, and wheat, in the USA, Brazil, and EU would compete with land use and food production.
- Biomass feedstock must be in excess after meeting biodiversity needs, e.g. nutrient retention in soil, feed for animals, etc.
- Excess or waste biomass feedstock if has sugar as one of the base-units, can be fermented to produce bioethanol.
- Integrated system must comprise: 1) pretreatment, enzymatic hydrolysis, fermentation and bioethanol purification, Section 2) wastewater treatment and anaerobic digestion and Section 3) combined heat and power (CHP) system, to be self-sustainable.
- Self-sustainability of the plant means onsite enzyme production, combined heat and power generation and water recovery, serving two purposes: meeting on-site utility and raw material needs and maximising potential for multi-productions.
- Also, bioethanol purification to a high grade is essential.

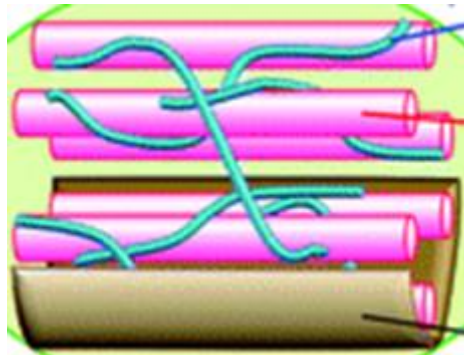
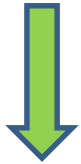
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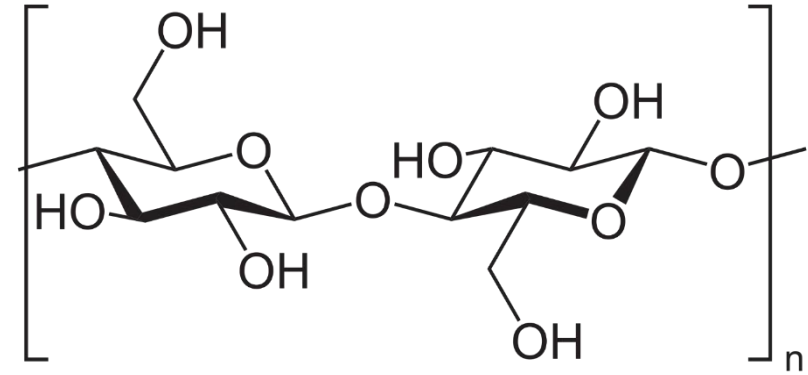
Sustainability

- Technical challenges: we have to ensure electricity coproduction with bioethanol as main product where possible to maximise energy efficiency. Biochemical reactions have low conversions and yield. Biomass contains moisture which gives rise to a dilute fermentation broth. Water and ethanol form azeotrope that requires energy intensive distillation steps to recover ethanol from dilute solution. The final separation step is adsorption based such as molecular sieve to produce high purity bioethanol. 1 mole of glucose is converted into equi-mass of bioethanol (2 moles; molar mass: 46) and carbon dioxide (2 moles; molar mass: 44) in the stoichiometric reaction, thus making glucose conversion to ethanol by mass to 51%.
- Environmental challenges: Biomass waste feedstock such as lignocelluloses availability including seasonality aspect and the volume of product bioethanol
- Economic challenges: Onsite production of enzyme, heat and electricity to meet in-process demands is essential for feasibility. Importing any of these means higher cost and economic infeasibility.
- Social challenges: Importing bioethanol to meet transport fuel demand means social cost especially from countries lower in the GDP per capita scale. There is dilemma however if foreign appreciation into less developing countries is avoided.

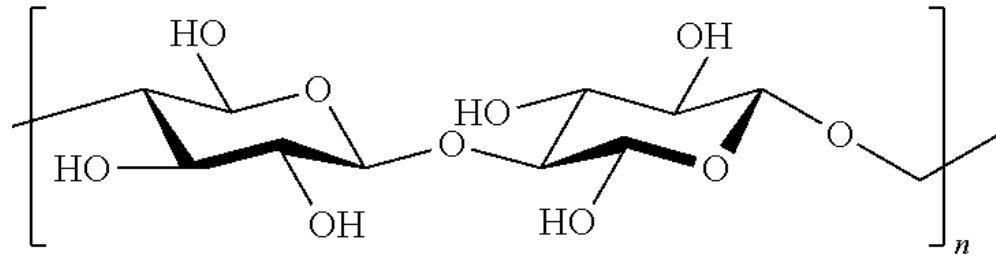
Lignocellulose Structure



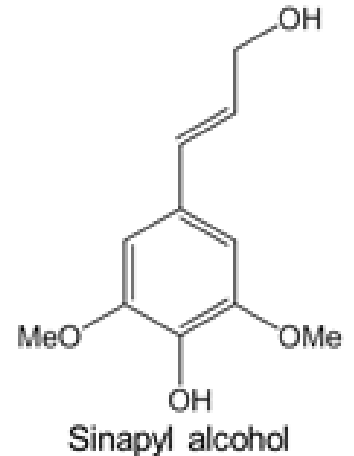
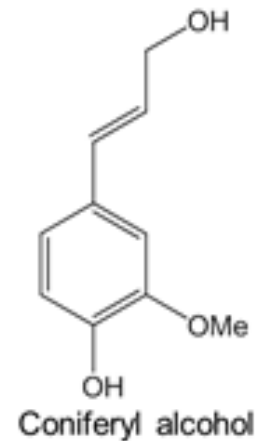
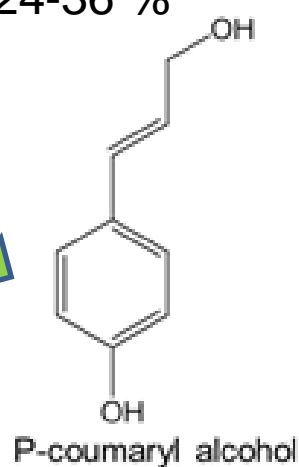
Cellulose 38-54 %



Hemicellulose 24-36 %

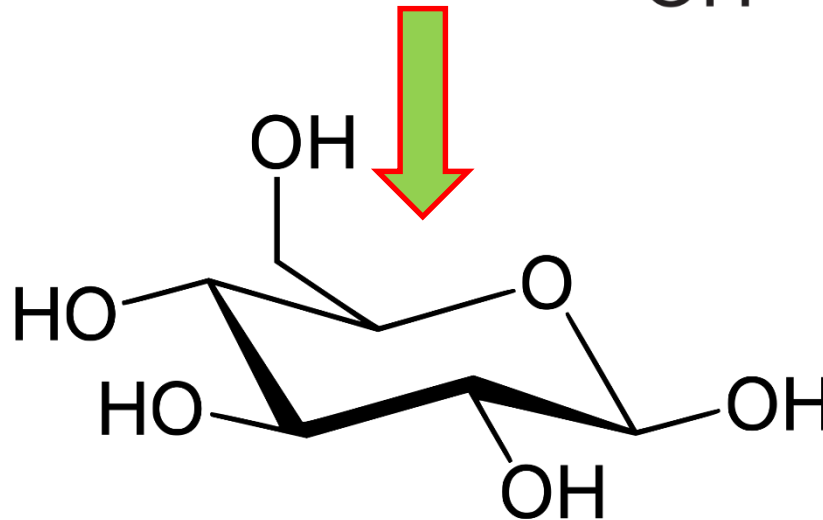
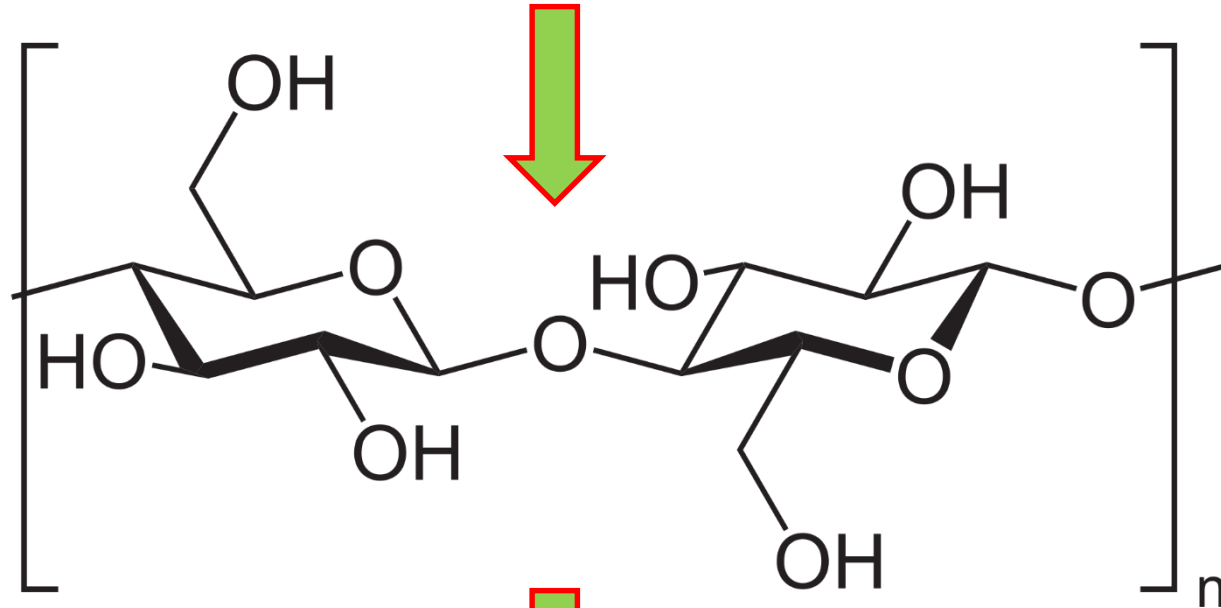


Lignin 15-25 %

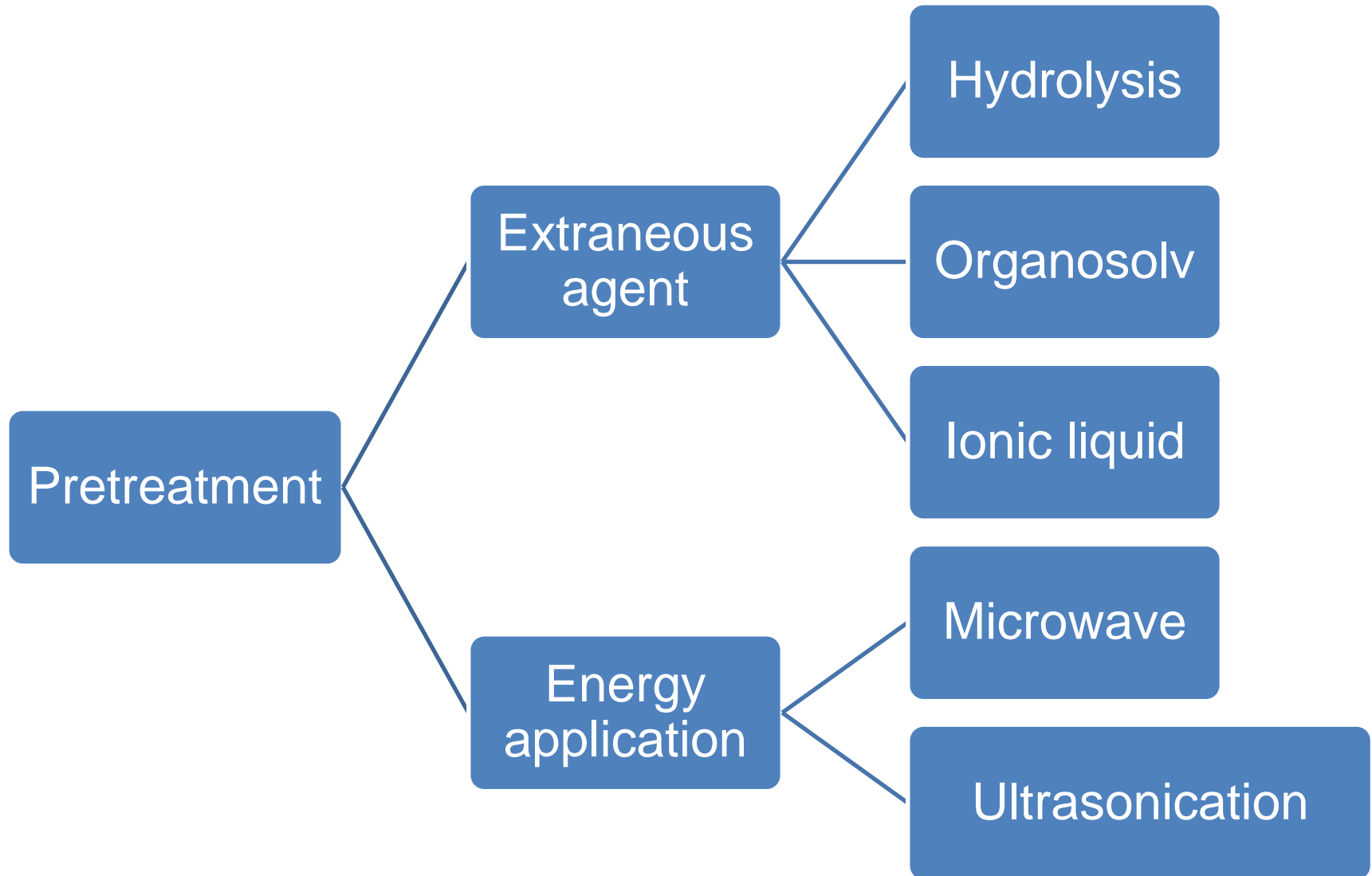


Cellulose Decomposition into Glucose

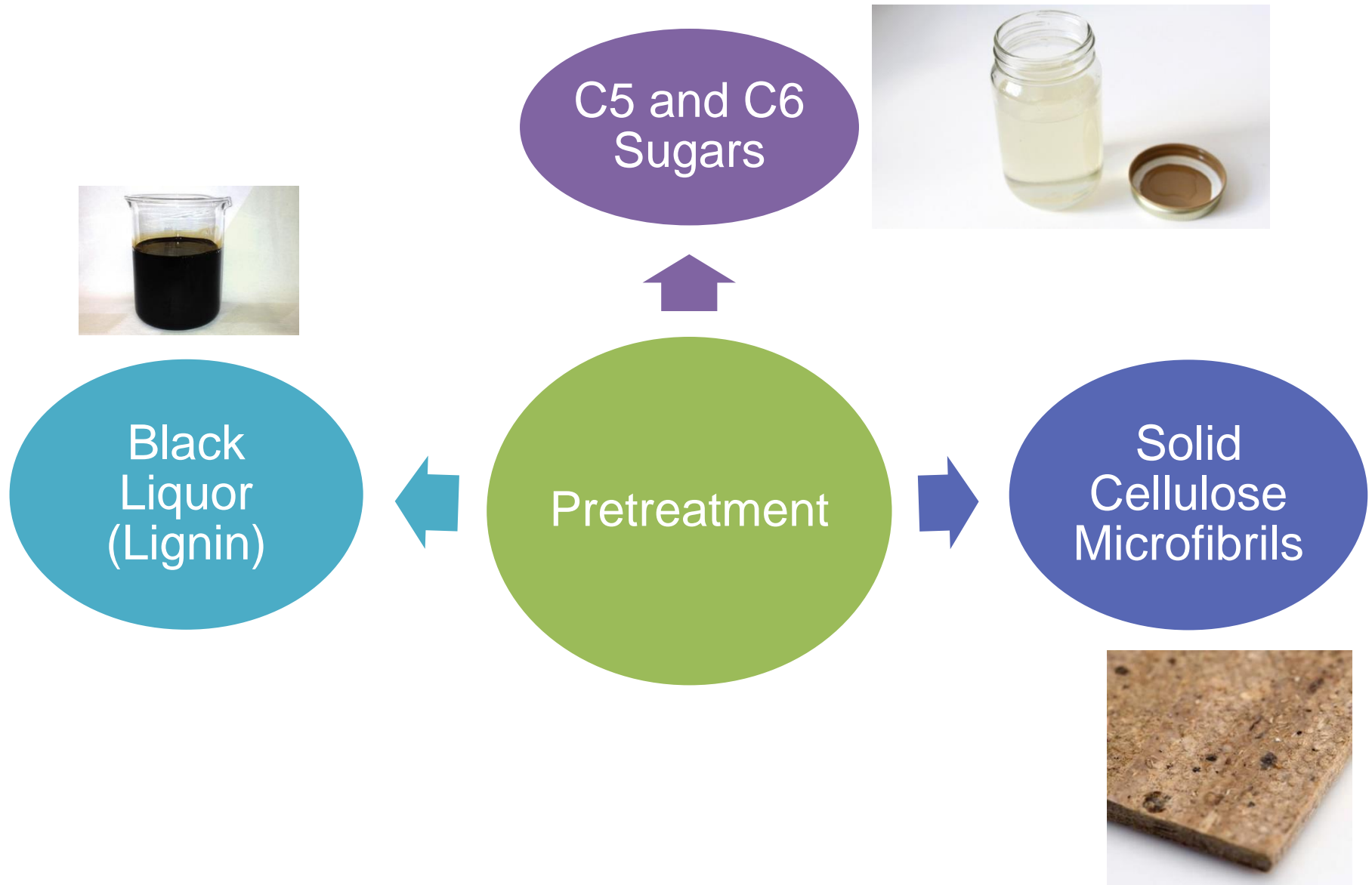
β -(1–4)-glycosidic bond



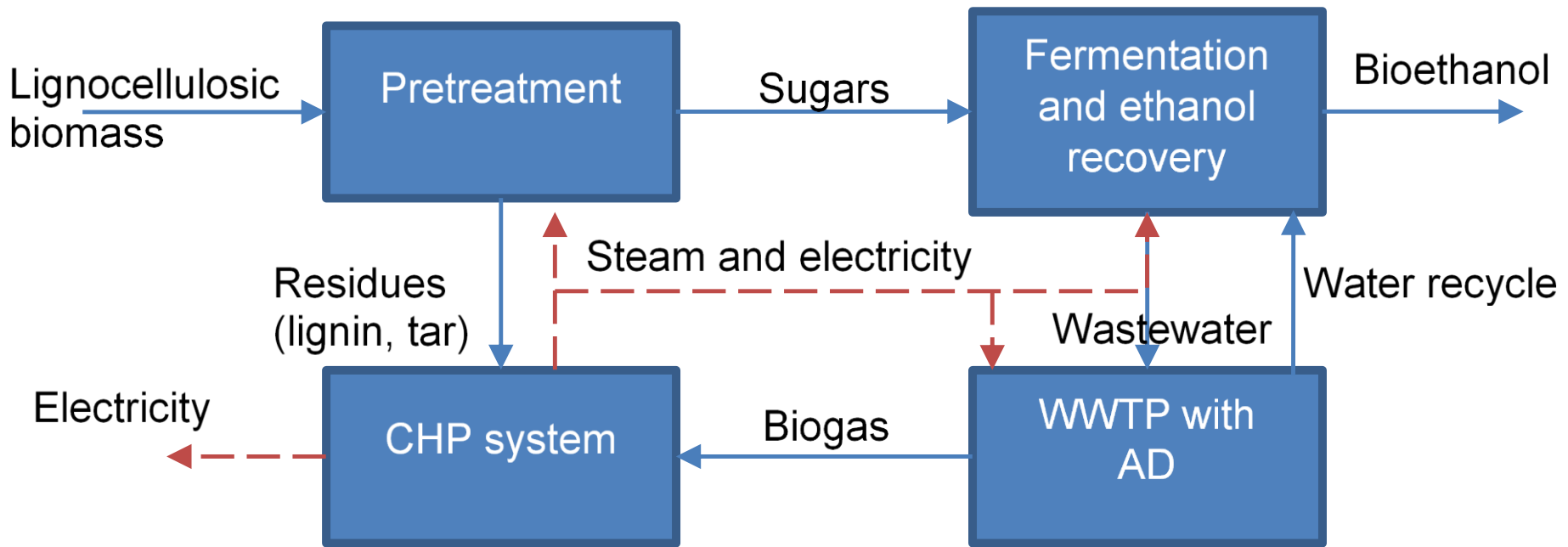
Lignocellulose Pretreatment



Lignocellulosic Platforms



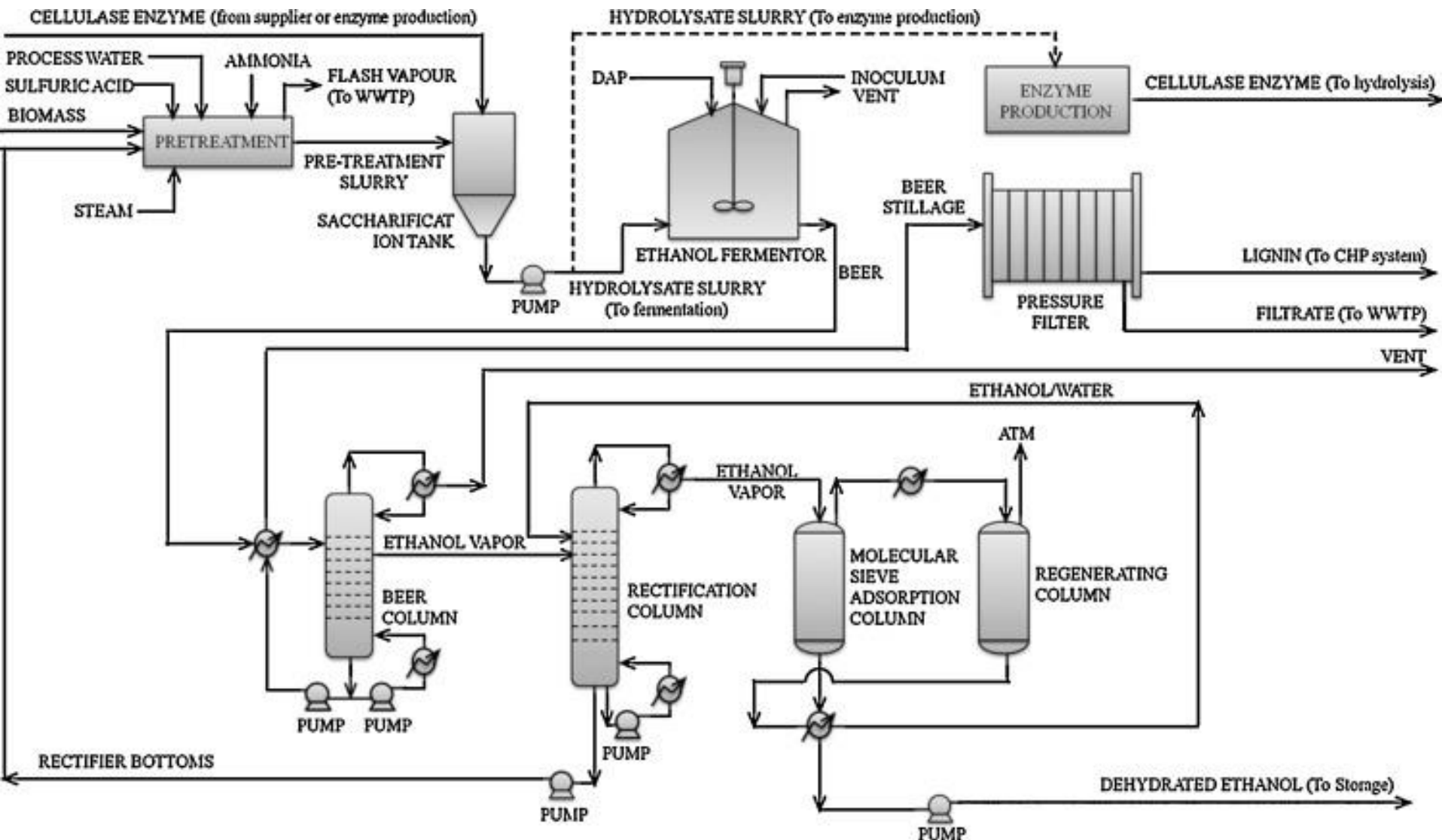
Block flow diagram of overall plant



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Bioethanol production train



Wan, Y.K., Sadhukhan, J., and Ng, D.K.S. (2016) Techno-economic evaluations for feasibility of sago biorefineries, Part 2: Integrated bioethanol production and energy systems. *Chemical Engineering Research & Design*, Special Issue on Biorefinery Value Chain Creation, 107, 102-116. <https://doi.org/10.1016/j.cherd.2015.09.017>

Key process description

- The main processes involved to convert the biomass into bioethanol are pretreatment, enzymatic hydrolysis, fermentation processes, and bioethanol recovery process.
- In the first stage of pretreatment process, biomass is fed to a pretreatment reactor and mixed with diluted sulphuric acid (18 mg acid/dry g of biomass) that catalyses the hydrolysis reaction at a temperature of 158°C.
- Steam at 13 bar is used in this stage to maintain the temperature.
- Most of the hemicellulose carbohydrates are converted into oligomers within a short residence time of 5 min.
- The resulting slurry goes into a second stage of pretreatment, oligomer conversion step, where most of the oligomers from the first stage are converted into C5 monomers at a temperature of 130°C and residence time of 20–30 min.
- The slurry is then flashed at atmospheric pressure. After the flash, the slurry containing 30 wt% of total solids is sent to a conditioning reactor, where water and ammonia are added to dilute the solid content to approximately 20 wt% and to increase the pH of the slurry to 5–6 to ensure miscibility for enzymatic hydrolysis.
- The slurry is cooled to 75°C after a total conditioning residence time of 30 min. Ammonia helps to avoid sugar losses and eliminate the solid–liquid separation steps. This makes ammonia a more economical alternative compared to lime due to reduced sugar loss and reduced capital cost.
- The flashed vapour is condensed and sent to WWTP.

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Fermentation

- After the hydrolysis process, the resulting slurry is cooled and fermented to bio-ethanol.
- In the fermentation process, recombinant co-fermenting bacterium (*Z. mobilis*) is used as fermenting microorganism or ethanologen.
- The ethanologen inoculums can be produced by mixing the slurry and nitrogen sources, i.e. Diammonium phosphate (DAP) in the fermenter. The main reactions are C6 and C5 sugar conversions into ethanol. The reaction catalysed by enzymes is thus a biochemical reaction.
- After the fermentation process, the fermentation broth has an ethanol concentration of 5.4%. It is then sent to distillation and molecular sieve adsorption for bioethanol recovery.

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Calculation stages

- Mass balance
- Energy analysis
- Economic analysis
- Environmental impact savings
- Social impact savings

An example of biomass composition

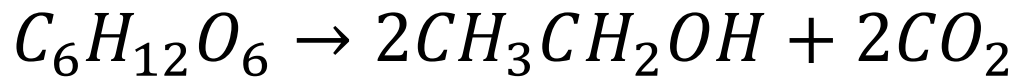
Wet analysis in % of waste wood.

Cellulose	29.4
Xylan	20.4
Glucan	4.8
Arabinan	0.5
Mannan	0.5
Galactan	0.5
Lignin	18.7
Ash	1.5
Moisture	23.7

Mass and energy balance correlations

$$\begin{aligned} Y_{bioethanol} &= 0.99 \times 0.51 \\ &\times [0.9 \times 0.85 \times 0.982 (X_{xylan} + X_{arabinan}) + 0.95 \\ &\times 0.97 (0.099 \times X_{glucan} + 0.912 \times X_{cellulose})] \end{aligned}$$

Fermentation is the process of decomposing an organic substrate into products (e.g. bioethanol) by bacteria, yeast, fungi and other microorganisms in gut. The reaction of bioethanol production from glucose fermentation is as follows (1 mole glucose is decomposed into 2 moles ethanol and 2 moles carbon dioxide):



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Mass and energy balance correlations

- $F_{AD} = 100 - X_{moisture} - X_{ash} - X_{lignin} - Y_{bioethanol}/0.51 - Y_{tar}$
- $Y_{tar} = 0.05 \times (X_{xylan} + X_{arabinan} + X_{mannan} + X_{galactan}) + 0.003 \times X_{glucan}$
- $Y_{biogas} = 0.3 \times F_{AD}$
- $E_{CHPin} = 23 \times Y_{biogas} + 23.5 \times X_{lignin} + 36 \times Y_{tar}$
- $Y_{steam} = 0.8 \times E_{CHPin} \times 0.77$
- $Y_{electricity} = 0.35 \times Y_{steam} - 4.74 \times Y_{bioethanol}$
- $\% \text{ Energy Efficiency} = (Y_{bioethanol} \times 29.7 + Y_{electricity}) / \text{Calorific value of biomass feedstock}$

Economic Analysis

- **Economic Margin** = Value of products – Operating cost – Capital cost
- **Netback** (when feedstock cost is unknown) = Value of products – Operating cost w/o Cost of feedstock – Capital cost
- **Cost of production** (when product price is unknown) = Operating cost + Capital cost

Cost components

- Capital cost (Annual)
 - Delivered cost of equipment
 - Direct
 - Indirect
 - Working capital
 - Total capital investment
 - Annual capital charge (assume 13%)
- Operating cost
 - Fixed
 - Variable

Correlation between delivered cost of equipment and size

$$\frac{\text{COST}_{\text{size2}}}{\text{COST}_{\text{size1}}} = \left(\frac{\text{SIZE}_2}{\text{SIZE}_1} \right)^R$$

where

SIZE₁ is the capacity of the base system, t/h or t/y,

SIZE₂ is the capacity of the system after scaling up/down, t/h or t/y,

COST_{size1} is the cost of the base system, €,

COST_{size2} is the cost of the system after scaling up/down, €,

R is the scaling factor.

Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis, First Edition.
Jhuma Sadhukhan, Kok Siew Ng and Elias Martinez Hernandez.

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Companion Website: <http://www.wiley.com/go/sadhukhan/biorefineries>

Apply Capital Cost Index

$$C_{pr} = C_o \left(\frac{I_{pr}}{I_o} \right)$$

where

C_{pr} is the present cost.

C_o is the original cost.

I_{pr} is the present index value.

I_o is the original index value.

Process unit	Base Cost				Base Year	Cost Index	Cost Index in year 2014	Installation Factor
	(million \$)	Base size	Capacity or base size unit	scale factor				
Pretreatment								
Mechanical	4.44	83.3	dry t/h biomass feed	0.67	2003	402	574.4	2
Dilute acid treatment	14.1	83.3	dry t/h biomass feed	0.78	2003	402	574.4	2.36
Hydrolysis and Fermentation	0.26	3.53	t/h product bioethanol	0.6	2003	402	574.4	2.2
Bioethanol recovery								
Distillation	2.96	18.466	t/h product bioethanol	0.7	2003	402	574.4	2.75
Molecular sieve	2.92	18.466	t/h product bioethanol	0.7	2003	402	574.4	1
Wastewater treatment								
Solids separation	1.05	10.1	dry t/h organics	0.65	2003	402	574.4	2.2
(An)aerobic digestion	1.54	43	t/h wastewater including organics	0.6	2003	402	574.4	1.95
Total cost of storage and CHP system	116360501 \$							

Capital cost

Plant	Solid Processing	Solid–Fluid Processing	Fluid Processing
<i>Direct Cost</i>			
Delivered cost of equipment	1.00	1.00	1.00
Installation	0.45	0.39	0.47
Instrumentation and control	0.18	0.26	0.36
Piping	0.16	0.31	0.68
Electrical systems	0.10	0.10	0.11
Buildings (including services)	0.25	0.29	0.18
Yard improvements	0.15	0.12	0.10
Service facilities	0.40	0.55	0.70
Total direct cost, C_D	2.69	3.02	3.60
<i>Indirect Cost</i>			
Engineering and supervision	0.33	0.32	0.33
Construction expenses	0.39	0.34	0.41
Legal expenses	0.04	0.04	0.04
Contractor's fee	0.17	0.19	0.22
Contingency	0.35	0.37	0.44
Total indirect cost, C_{ID}	1.28	1.26	1.44
Working capital	0.7	0.75	0.89
Total capital investment, C_{TCI}	4.67	5.03	5.93

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Annual capital cost

Total capital investment $\times 0.13$

Operating cost

Fixed operating cost dependent on indirect capital cost

Maintenance	5-10%	of indirect capital cost (annualised)
Capital charges	10%	of indirect capital cost (annualised)
Insurance	1%	of indirect capital cost (annualised)
Local taxes	2%	of indirect capital cost (annualised)
Royalties	1%	of indirect capital cost (annualised)

Fixed operating cost dependent on personnel cost

Personnel	52033	\$ per t/h product bioethanol
Laboratory costs	20%	of personnel cost
Supervision	20%	of personnel cost
Plant overheads	50%	of personnel cost

Total fixed operating cost = Fixed operating cost dependent on indirect capital cost + Fixed operating cost dependent on personnel cost

Total operating cost = $1.3 \times (\text{Total fixed operating cost} + \text{Variable operating cost})$

Indirect capital cost

To calculate the fixed operating cost, indirect capital cost must be known, shown as follows:

Indirect Capital Cost

Item	Factor	
Engineering and supervision	0.32	
Construction expenses	0.34	
Legal expenses	0.04	
Contractor's fee	0.19	
Contingency	0.37	
Total	1.26	Times annualised Delivered cost of equipment

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Variable operating cost

Inventory	kg per t product bioethanol	\$/kg inventory
Sulphuric acid (0.93 w/w)	64.7	0.09
Ammonia	34.7	0.44
DAP	3.7	0.97
Caustic	17.5	0.15
Lime	1.5	0.2
Electricity	price in \$/kWh	0.14
Heat	price in \$/kWh	0.05

Do not forget to consider the cost of biomass!

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Environmental impact savings

- In the current policy landscape, the final use of biomass for energy and transportation fuel is considered to be carbon neutral. This is because direct biogenic emissions from biomass end use are captured during growth completing the carbon cycle.
- If energy needed by biomass conversion process is supplied renewably e.g. by on-site generation, then emissions caused by burning fossil derived transportation fuel can be eliminated by using biofuel.
- Savings in various life cycle impact categories can be estimated from the difference in life cycle impacts between petrol and bioethanol for a given energy output.

Example of life cycle impact categories

Life cycle impact category	Unit (per GWh energy output)
Global warming potential	tonne CO ₂ equivalent
Acidification potential	tonne SO ₂ equivalent
Urban smog potential	tonne NMVOC equivalent
Eutrophication potential	tonne Phosphate equivalent
Fossil resource depletion potential	GJ

Social impact savings

- Social life cycle assessment (SLCA) estimates five main governing social categories, labour rights & decent work, health & safety, human rights, governance and community infrastructure.
- Among the different SLCA databases developed so far, the Social Hotspot Database (SHDB) is the most significant. Over a 5-years project, the New Earth involved stakeholders worldwide to assign importance and risk to each theme under each category in a sector of goods in a country. The supply chain interactions are considered in the computation of total index of a theme for a given sector in a given country. In constructing the SHDB, the team combined the Global Trade Analysis Project (GTAP) data on import-export of goods between countries and social risk characterisation data (from stakeholders) to calculate social attributional risks of products in two ways, countries of origin and life cycle approaches.
- The unit of risks is medium-risk hour (mrh) for a given functional unit, e.g. rate of product formation in case of a production system, in terms of its monetary value worth.
- The individual social theme risks are factored by the netted fractional imports considering the entire supply chain and these factored individual social theme risks are added to give a total social theme risk for given sector in given country to create a base case.
- Using the UNCOMTRADE data and the SHDB, a base case scenario and a scenario with 100% self-generation case (or no import) are compared in terms of weighted aggregated risks in social categories for a country, in the TESARREC platform.

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SLCA results: UK case

	Labor Rights & Decent Work	Health & Safety	Human Rights	Govern ance	Community Infrastructure
Belgium	0.52	0.24	0.13	0.16	0.14
Bolivia	28.71	4.85	1.60	10.23	10.05
Brazil	2.51	2.70	0.81	0.48	0.34
Canada	0.01	0.00	0.00	0.00	0.00
Costa Rica	0.06	0.03	0.00	0.01	0.00
Denmark	0.50	0.44	0.12	0.09	0.06
France	0.00	0.00	0.00	0.00	0.00
Germany	12.01	9.88	2.73	2.62	3.28
Guatemala	33.49	3.36	7.58	11.14	1.57
Hungary	1.60	1.50	0.28	0.62	0.39
Ireland	0.23	0.12	0.05	0.04	0.03
Italy	0.06	0.06	0.02	0.02	0.01
Mexico	0.90	0.25	0.26	0.38	0.04
Netherlands	0.00	0.00	0.00	0.00	0.00
Peru	180.38	70.35	13.41	37.20	53.72
Philippines	39.50	21.43	13.35	16.61	7.04
Poland	0.00	0.00	0.00	0.00	0.00
Romania	0.01	0.01	0.00	0.00	0.01
Spain	0.00	0.00	0.00	0.00	0.00
Sweden	1.13	1.39	0.25	0.25	0.17
Ukraine	0.08	0.03	0.01	0.03	0.01
United Kingdom	0.01	0.01	0.00	0.00	0.00
USA	0.00	0.00	0.00	0.00	0.00

SLCA results: Mexico case

	Labor Rights & Decent Work	Health & Safety	Human Rights	Governance	Community Infrastructure
Brazil	0.11	0.12	0.04	0.02	0.02
Canada	0.08	0.05	0.01	0.02	0.01
France	0.12	0.12	0.03	0.03	0.03
Germany	0.05	0.04	0.01	0.01	0.01
Guatemala	481.23	48.29	108.88	160.12	22.53
USA	128.45	30.44	16.06	20.42	10.33
Mexico	96.03	-9.37	40.27	39.20	156.41

Benchmark Study References

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