Produção de ETANOL

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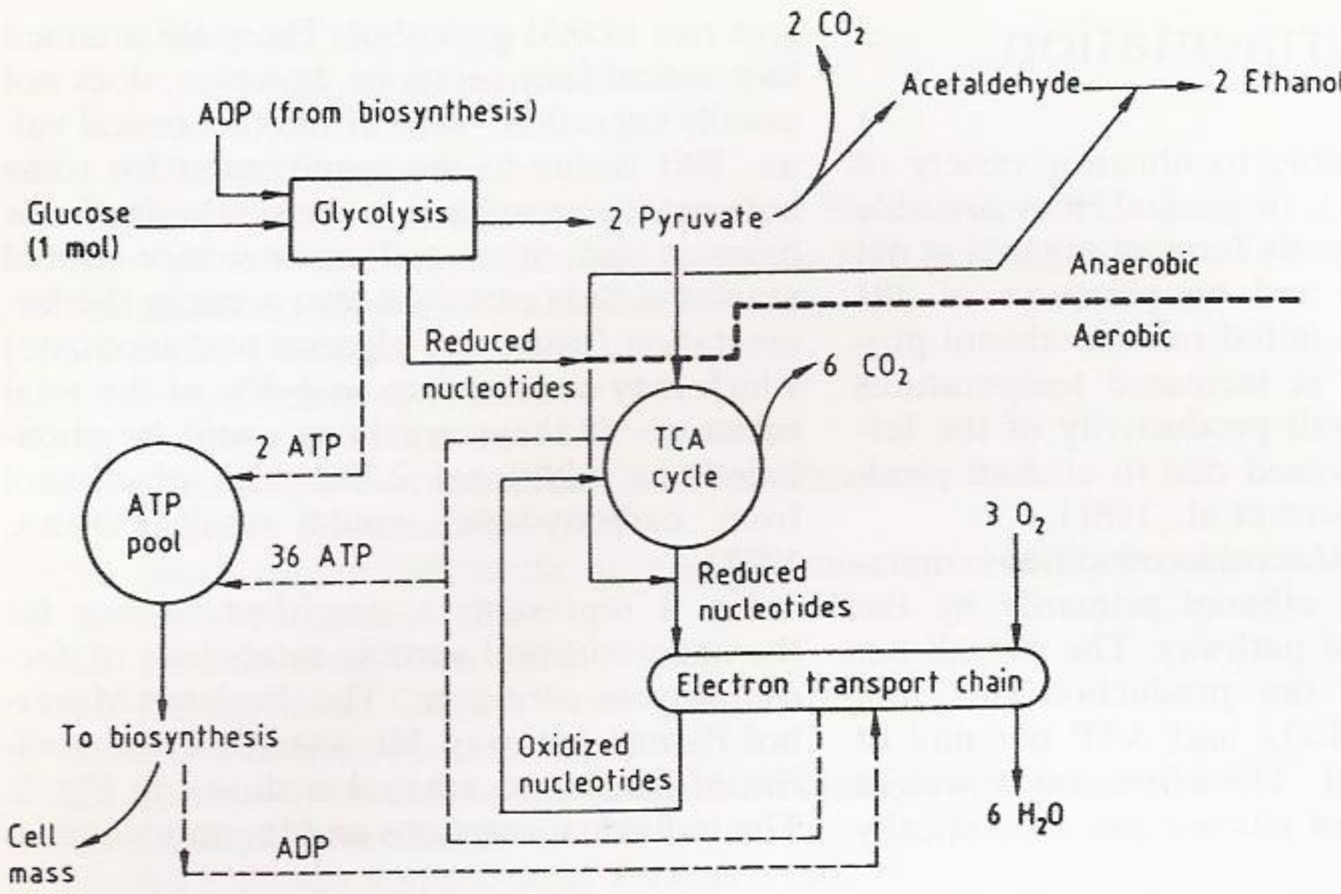


Fig. 1. Simplified chart of anaerobic and aerobic catabolism of *Saccharomyces cerevisiae* ADP: adenosine diphosphate; ATP: adenosine triphosphate; TCA: tricarboxylic acid (citric acid).

Table 1. The Ability of *Saccharomyces* and *Kluyveromyces* Species to Ferment Sugars (Source: JONES et al., 1981)

Carbon Number of Basic Subunit	Type of Basic Subunit	Sugar	Basic Unit	Yeasts		
				S. cerevisiae	*S. uvarum (carlsbergensis)*	*Kluyveromyces fragilis*
Six carbon sugars	aldose sugars	glucose	glucose	+	+	+
		maltose	glucose	+	+	−
		maltotriose	glucose	+	+	−
		cellobiose	glucose	−	−	−
		trehalose	glucose	+/−	+/−	−
		galactose	galactose	+	+	+
		mannose	mannose	+	+	+
		lactose	glucose, galactose	−	−	+
		melibiose	glucose, galactose	−	+	
	ketose sugars	fructose	fructose	+	+	+
		sorbose	sorbose	−	−	−
	aldoses and ketoses	sucrose	glucose, fructose	+	+	+
		raffinose	glucose, fructose galactose	+/−	+	+/−
	deoxy-sugars	rhamnose	6-deoxymannose	−	−	−
		deoxyribose	2-deoxyribose	+/−	+/−	+/−
Five carbon sugars	aldose sugars	arabinose	arabinose	−	−	−
		xylose	xylose	−	−	−

Table 2. Inhibition Kinetic Constants Associated With Data Produced By Various Workers (Source: HOPPE and HANSFORD, 1982)

	Added Ethanol			Autogenous Ethanol		
	EGAMBERDIEV and IERUSALIMSKII (1968)	AIBA and SHODA (1969)	BAZUA and WILKE (1977)	PIRONTI (1971)	CYSEWSKI (1976)	HOPPE and HANSFORD (1982)
°C	28	30	35	30	35	30
μ_{max} (h^{-1})[a]	0.31	0.43	0.64	0.26	0.58	0.64
K_s ($g\,L^{-1}$)[b]	—	—	0.24	15.5	4.9	3.3
K_p ($g\,L^{-1}$)[c]	20.6	55	40	13.7	5.0	5.2
$Y_{p/s}$[d]	0.39	0.35	0.52	0.47	0.44	0.43

[a] Maximum specific growth rate, [b] substrate saturation constant, [c] product inhibition constant, [d] product yield coefficient

Tab. 4. Bacterial Species Producing Ethanol as the Main Fermentation Product (WIEGEL, 1980)

Mesophilic Organisms		mmol Ethanol Produced per mmol Glucose Metabolized
Clostridum sporogenes		up to 4.15[a]
Clostridium indolis (pathogenic)		1.96[a]
Clostridium sphenoides		1.8[a] (1.8)[b]
Clostridium sordelli (pathogenic)		1.7
Zymomonas mobilis (syn. *anaerobica*)		1.9 (anaerobe)
Zymomonas mobilis ssp. *pomaceae*		1.7
Spirochaeta aurantia		1.5 (0.8)
Spirochaeta stenostrepta		0.84 (1.46)
Spirochaeta litoralis		1.1 (1.4)
Erwinia amylovora		1.2
Leuconostoc mesenteroides		1.1
Streptococcus lactis		1.0
Sarcina ventriculi (syn. *Zymosarcina*)		1.0
Thermophilic Organisms	T_{max} [°C]	**mmol Ethanol Produced per mmol Glucose Utilized**
Thermoanaerobacter ethanolicus (gen. nov.)	78	1.9
Clostridum thermohydrosulfuricum	78	1.6
Bacillus stearothermophilus	78	1.0 (anaerobic above 55°C)
Thermoanaerobium brockit	78	0.95
Clostridium thermosaccharolyticum (syn. *tartarivorum*)	68	1.1
Clostridium thermocellum (*thermocellulaseum*)	68	1.0

[a] In the presence of high amounts of yeast extract.
[b] Values in brackets were obtained with resting cells.

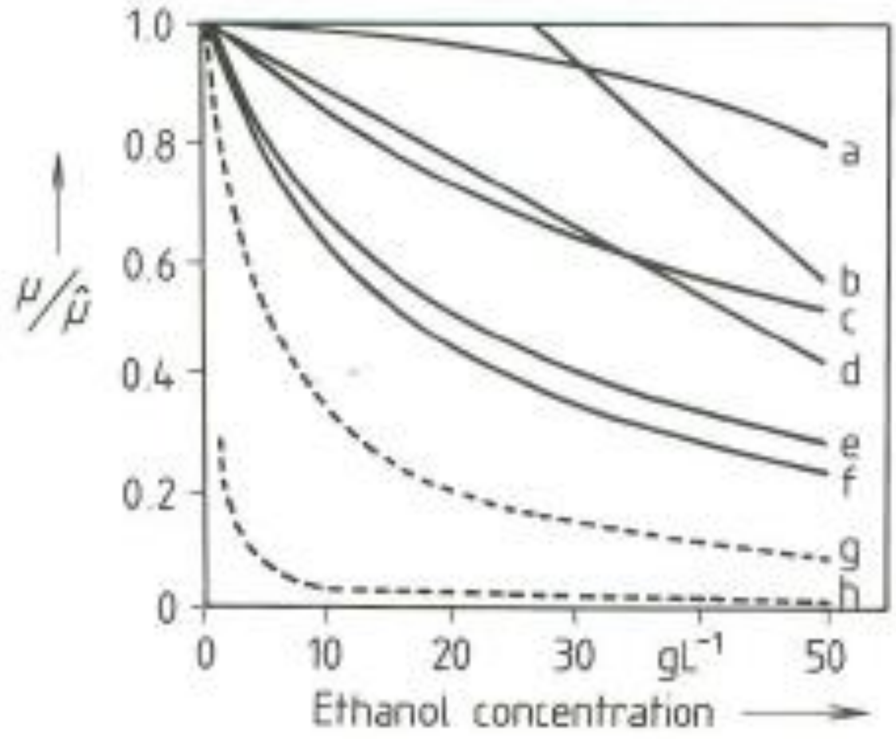


Figure 1. Comparison of the effect of various ethanol inhibition functions. Source: HOPPE and HANSFORD (1982). – μ specific growth rate, $\hat{\mu}$ maximum specific growth rate, a BAZUA and WILKE (1977), continuous, b HOLZBERG et al. (1967), batch, c AIBA and SHODA (1969), continuous, d GHOSE and TYAGI (1979a) continuous, e EGAMBERDIEV and IERUSALIMSKII (1968), batch, f AIBA and SHODA (1969), batch, g HOPPE (1981), continuous, h STREHAIANO et al. (1978), batch. Source of ethanol: —— added. ---- autogenous.

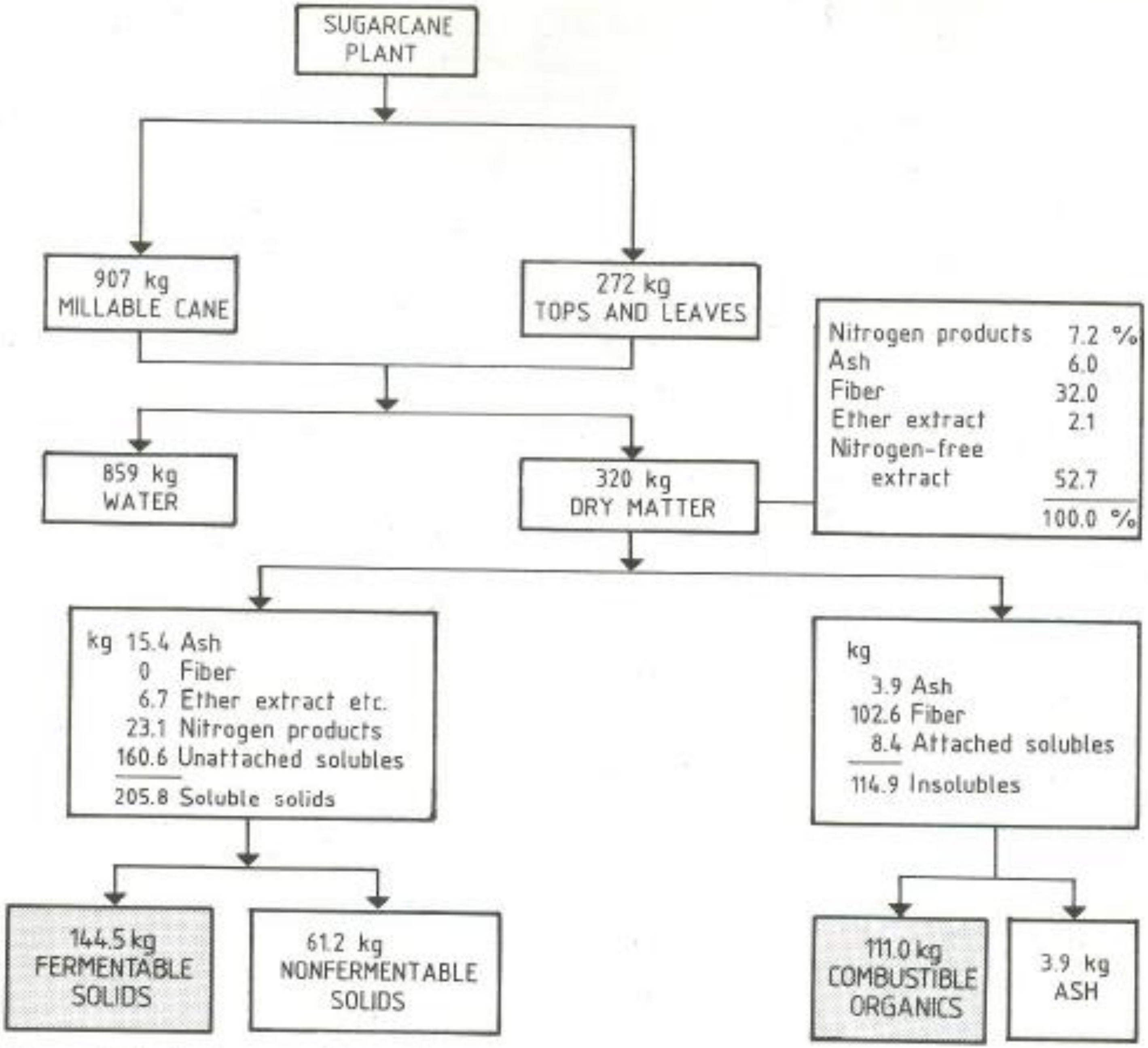


Figure 2. Typical composition of sugarcane. Source: NATHAN (1978). – Fermentable solids include sucrose, starches, and various other carbohydrates. Products in shaded boxes are usable for fuel.

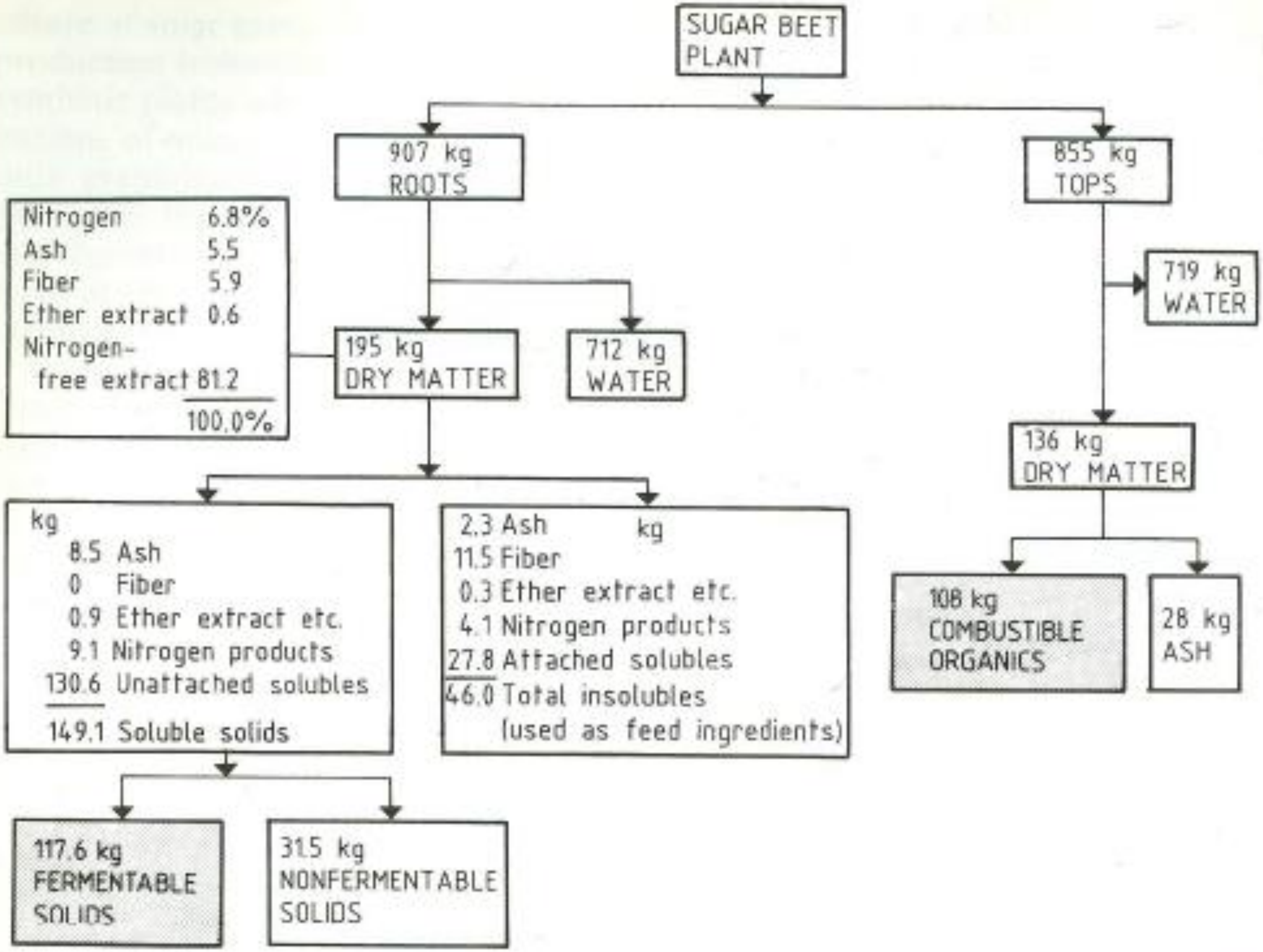


Figure 3. Typical composition of sugar beets. Source: NATHAN (1978). – Fermentable solids include sucrose, starches, and various other carbohydrates. Products in shaded boxes are usable for fuel.

Table 3. Cane and Beet Molasses – Principal Values at 75% Dry Matter (Source: BAKER, 1979)

		cane	beet
Total sugars	%	48/56	48/52
Non sugar organic matter	%	9/12	12/17
Sulfated ash	%	10/15	10/12
Total organic matter[a]	%	60/65	63/65
Protein i.e. N × 6.25	%	2/4	6/10
Sodium	%	0.1/0.4	0.3/0.7
Potassium	%	1.5/5.0	2.0/7.0
Calcium	%	0.4/0.8	0.1/0.5
Chlorine	%	0.7/3.0	0.5/1.5
Phosphorus	%	0.6/2.0	0.02/0.07
Biotin	mg/kg	1.2/3.2	0.04/0.13
Folic acid	mg/kg	ca. 0.04	ca. 0.2
Inositol	mg/kg	ca. 6000	5800/8000
Ca-pantothenate	mg/kg	54/6.5	50/100
Pyridoxine	mg/kg	2/6.5	ca. 5.4
Riboflavin	mg/kg	ca. 2.5	ca. 0.4
Thiamine	mg/kg	ca. 1.8	ca. 1.3
Nicotinic acid	mg/kg	20/800	20/45
Choline	mg/kg	600/800	400/600

[a] Total organic matter is total solids less sulfated ash

Table 4. Chemical Composition of Organic Dry Substance in a Spent Spruce Sulfite Liquor (in percent) – Source: DETROY and HESSELTINE (1978)

Lignosulfonic acids	43
Hemilignin compounds	12
Incompletely hydrolyzed hemicellulose compounds and uronic acids	7
Monosaccharides	
D-Glucose	2.6
D-Xylose	4.6
D-Mannose	11.0
D-Galactose	2.6
L-Arabinose	0.9
Acetic acid	6
Aldonic acids and substances not investigated	10

Table 5. Comparison of Sweet and Acid Whey Composition (Source: DREWS, 1975)

Components	Composition in Sweet Whey (%)	Composition in Acid Whey (%)
Dry matter	6-7	5-6
Ash	0.5-0.7	0.7-0.8
Crude protein	0.8-1.0	0.8-1.0
Nitrogenous compounds as % of total nitrogen		
genuine protein	52.5	43.9
peptides	31.3	33.1
amino acid	2.5	6.1
creatin	2.6	2.5
ammonia	1.0	2.3
urea	9.1	10.3
purines	1.0	1.8
Lactose	4.5-5.0	3.8-4.2
Lactic acid	traces	up to 0.8
Citric acid	0.1	0.1
pH	4.5-6.7	3.9-4.5

Table 6. Representative Fruit and Vegetable Processing Wastes in the United States – Source: COOPER (1976)

Product and Process Employed	Major Season	Residuals Wet Weight (t/a)	Residual Carbohydrate Content (tons d.w.) extractable	crude fiber	Percent Disposed (not used in by-product manufacture)
Apple	Aug.–Jan.				
peel and core (69%)		284400	38376	2840	31
crush (31%)		42600	5924	1573	
Citrus	all year	3555640	944378	204805	3
crush (100%)					
Grape	Aug.–Nov.	438000	54750	56940	20
crush (100%)					
Peach	July–Oct.	192500	86625	28875	68
peel and pit (100%)					
Beet	July–Dec.	98666	7891	3946	80
peel and trim (100%)					
White potatoes	all year	2595400	410073	36335	9
Tomato	July–Nov.	70200	1543	1051	78
peel (10%)					
crush (90%)					

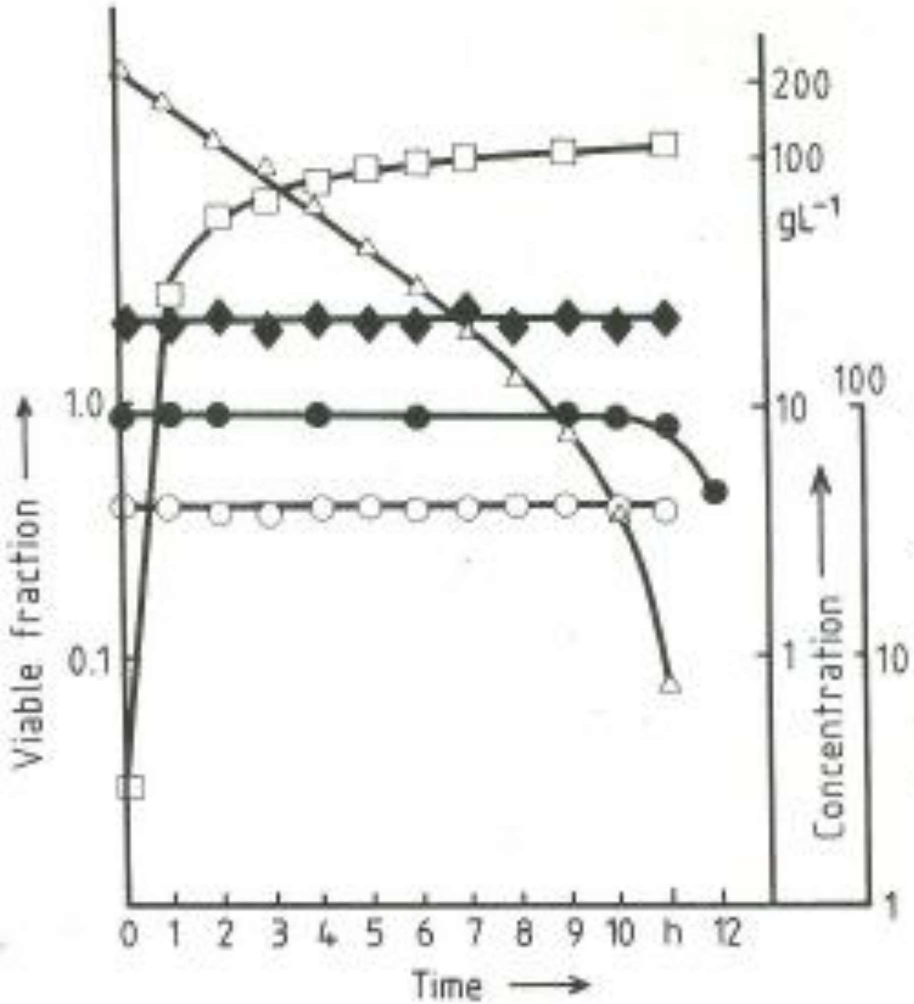


Figure 4. Batch fermentation of bagasse hydrolysate (from GHOSE and TYAGI (1979a). – ◆ Dry weight of yeast cells (g/L); ● viable fraction of cells; ○ Optical density; □ EtOH concentration (g/L); △ glucose concentration (g/L). Initial cell concentration is 23.6 g/L; initial glucose concentration is 220 g/L.

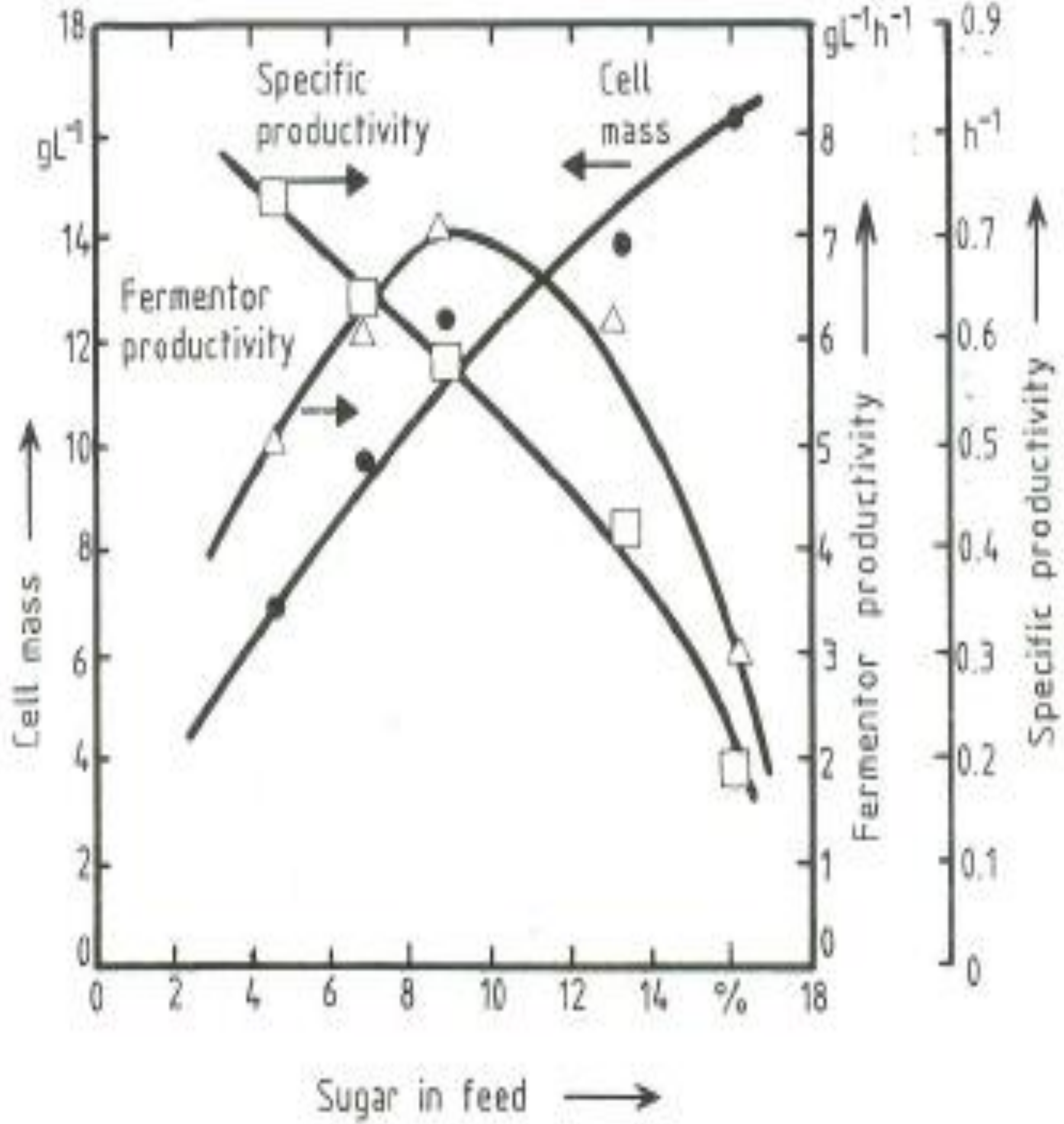


Figure 5. Effect of glucose concentration on continuous fermentation.
Source: Cysewski and Wilke (1978). – Conditions at "complete" substrate utilization.

Table 7. Industrial Productivity of Alternative Fermentation Systems Utilizing Yeasts – Adapted from VERGARA (1980)

System	Productivity (g EtOH/L/h)	TA[a]
Continuous, differential pressure, recycle (flash-ferm)	80	LS[b]
Continuous, vacuum, recycle	80	LS
Continuous, vacuum	40	LS
Continuous, recycle	40	D[c]
Rotor fermentor	36	LS
Batch, recycle	15	C[d]
Continuous, multi-stage	12	C
Continuous	5	C
Batch	2	C

[a] TA technology available [b] LS lab stage [c] D demonstration [d] C commercial

Table 8. Productivity Factors for Ethanol Production From Sugarcane. Source: LINDEMAN and ROCCHICCIOLI (1979)

	Alcohol Indirectly from Final Molasses	Alcohol Directly from Sugarcane Juice
Sugarcane yield in 1.5–2 year cycle (south-central region)	63 t/ha[a]	63 t/ha
Average sucrose yield (13.2 wt.%)	8.32 t/ha	8.32 t/ha
Crystal sugar production	7.0 t/ha	—
Final molasses or cane juice production	2.21 t/ha	66.2 t/ha
Fermentable sugars, molasses, or juices	1.32 t/ha	8.73 t/ha
Alcohol yield at 100% global efficiency	675 kg/ha	4460 kg/ha
Alcohol yield with reasonable 85% global efficiency	11.5 L/t cane or 730 L/ha	75 L/t cane or 4800 L/ha

[a] t metric ton; ha hectare

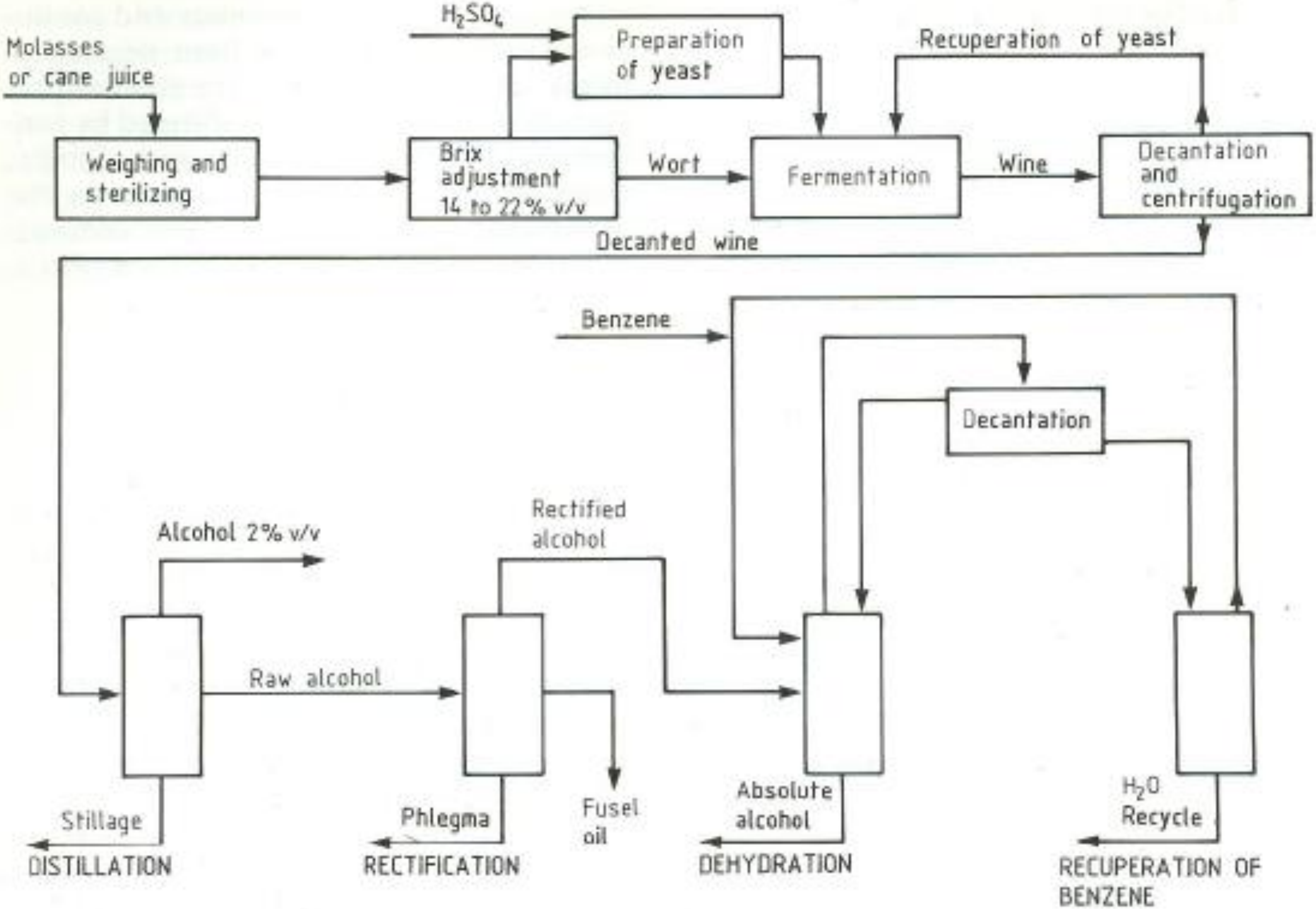


Figure 6. Block diagram for ethanol distillery. Source: LINDEMAN and ROCCHICCIOLI (1979).

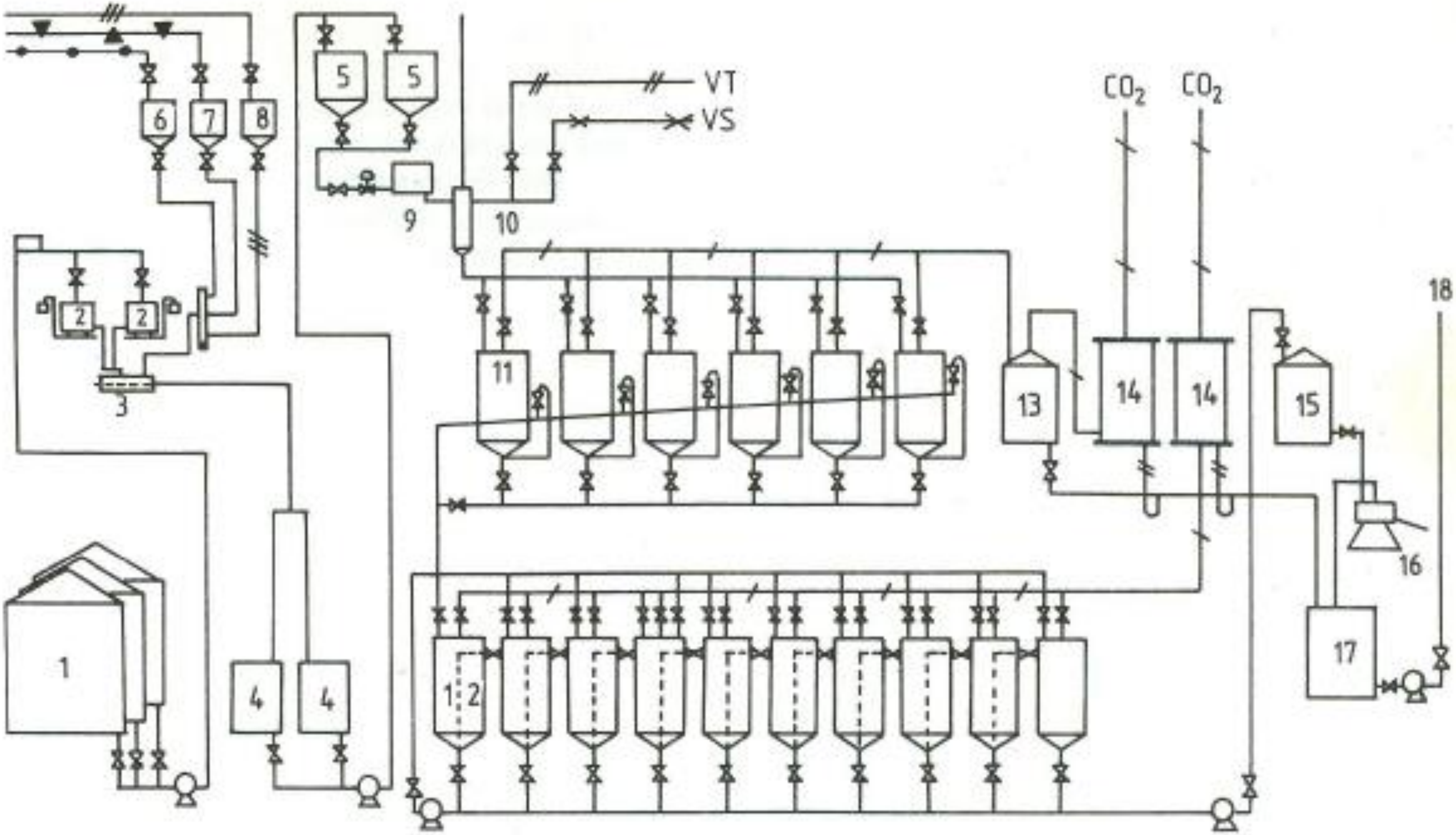


Figure 7. Flowsheet of continuous alcohol production from molasses. 1 molasses storage tank, 2 molasses scale, 3 mixing tank, 4 tank for chemical sterilization, 5 measuring tanks, 6 dosing of H_2SO_4, 7 dosing of chlorinated lime, 8 dosing of phosphoric acid, 9 flow meter, 10 diluting, 11 battery of yeast generators, 12 battery of fermentation tanks, 13 foam chamber, 14 alcohol chamber, 15 balance vessel, 16 separator, 17 storage tank for separated mash, 18 to distillation, VS cold water, VT hot water. Source: MALCHENKO et al. (1954).

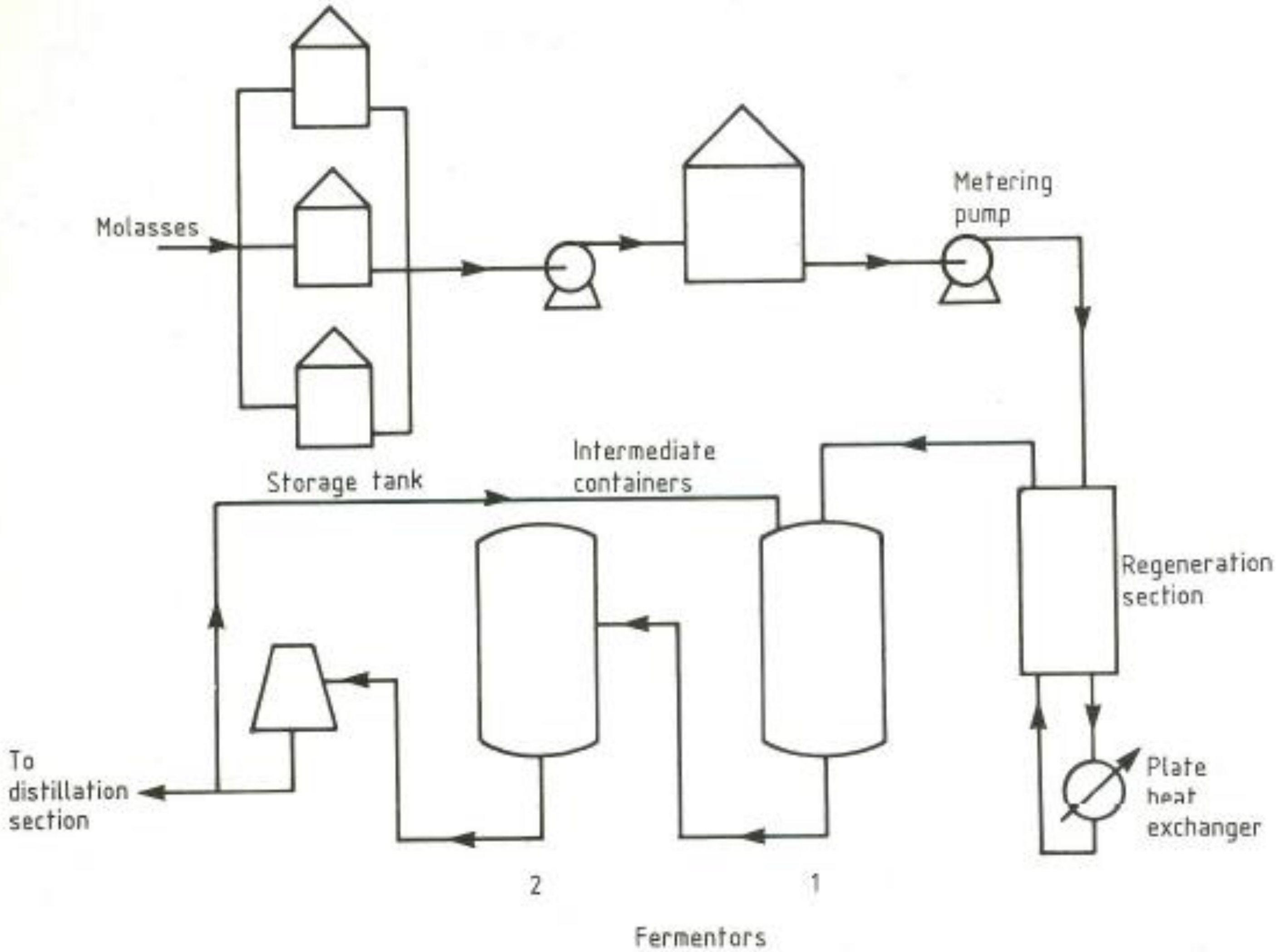


Figure 8. Continuous production of ethanol by the Danish Distilleries Ltd. Source: ROSEN (1978).

Aeração de 0,02 a 0,03 VVM no fermentador 1

Table 9. Performance Data for the Danish Distilleries Process - Source: ROSEN (1978)

	Fermentor 1[a]	Fermentor 2
Grams yeast, dry matter/liter	10	10
pH	4.7	4.8
Vol.% alcohol	6.1	8.4
% Residual sugar	1.0	0.1
Temperature, °C	35	35

[a] Residence time in each fermentor: 10.5 h. Afflux: 600 kg molasses diluted in 22×10^3 L h^{-1}.

65 litros de álcool por 100 kg de açúcares fermentescíveis

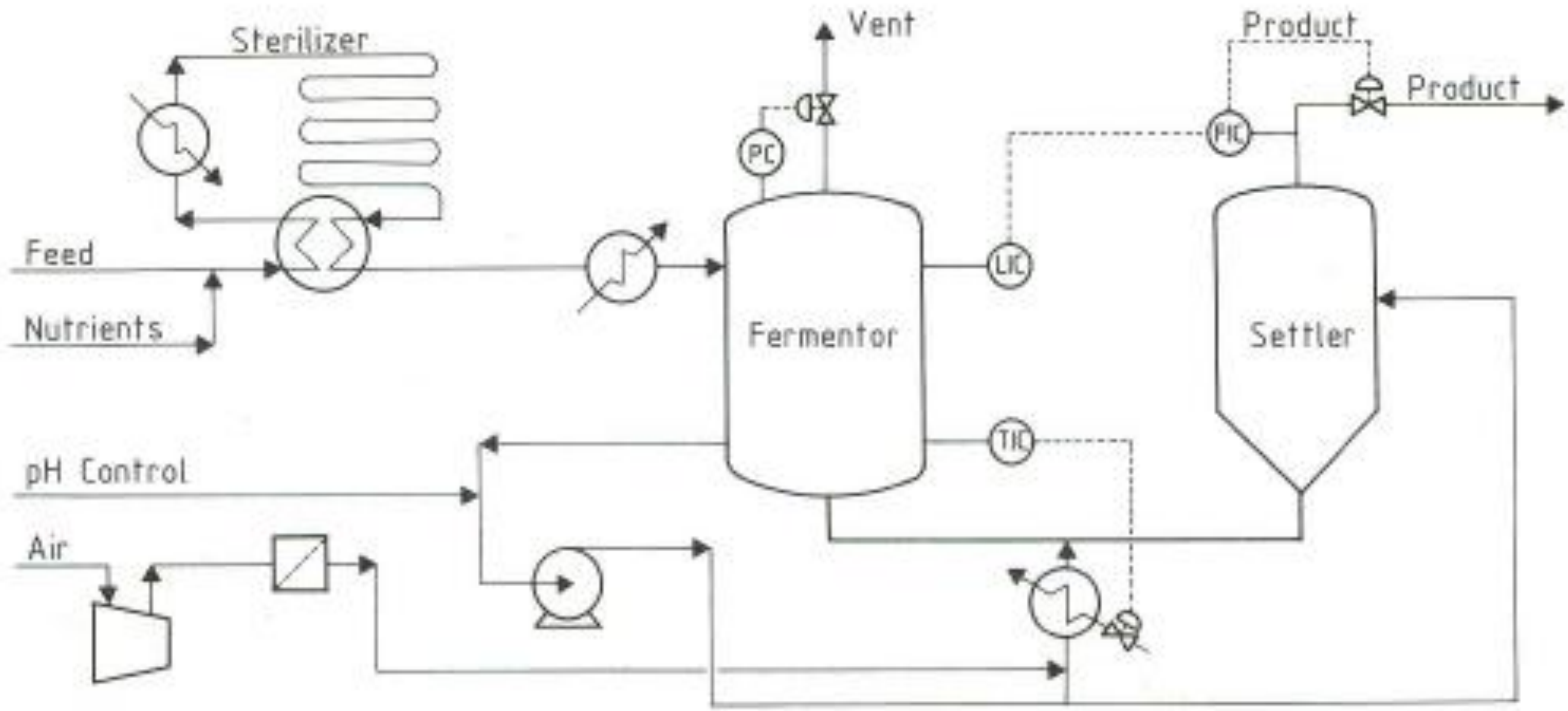


Figure 9. Flowsheet of the ALCON continuous fermentation process. – FIC flow indicating controller, LIC level indicating controller, TIC temperature indicating controller, PC pressure controller.

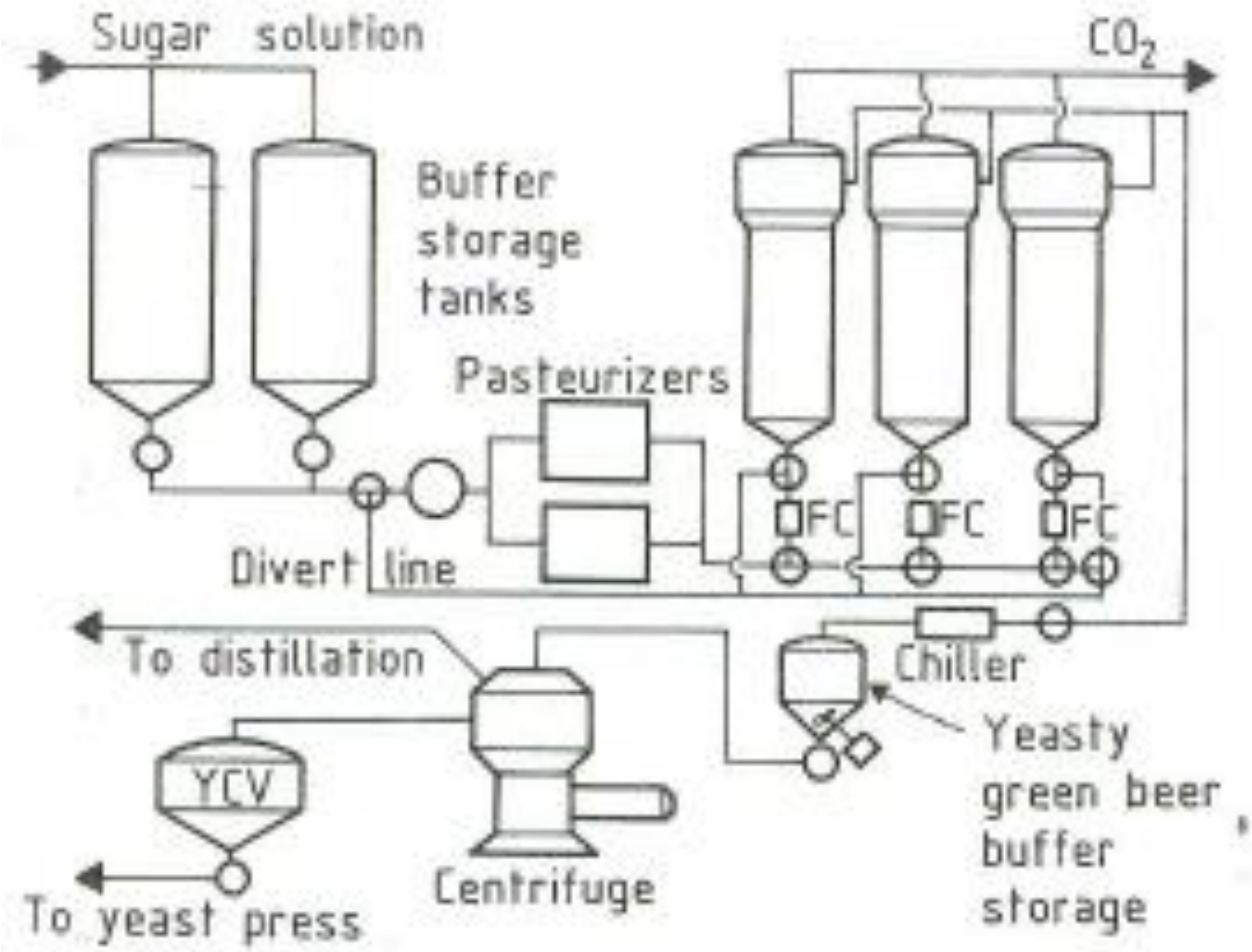


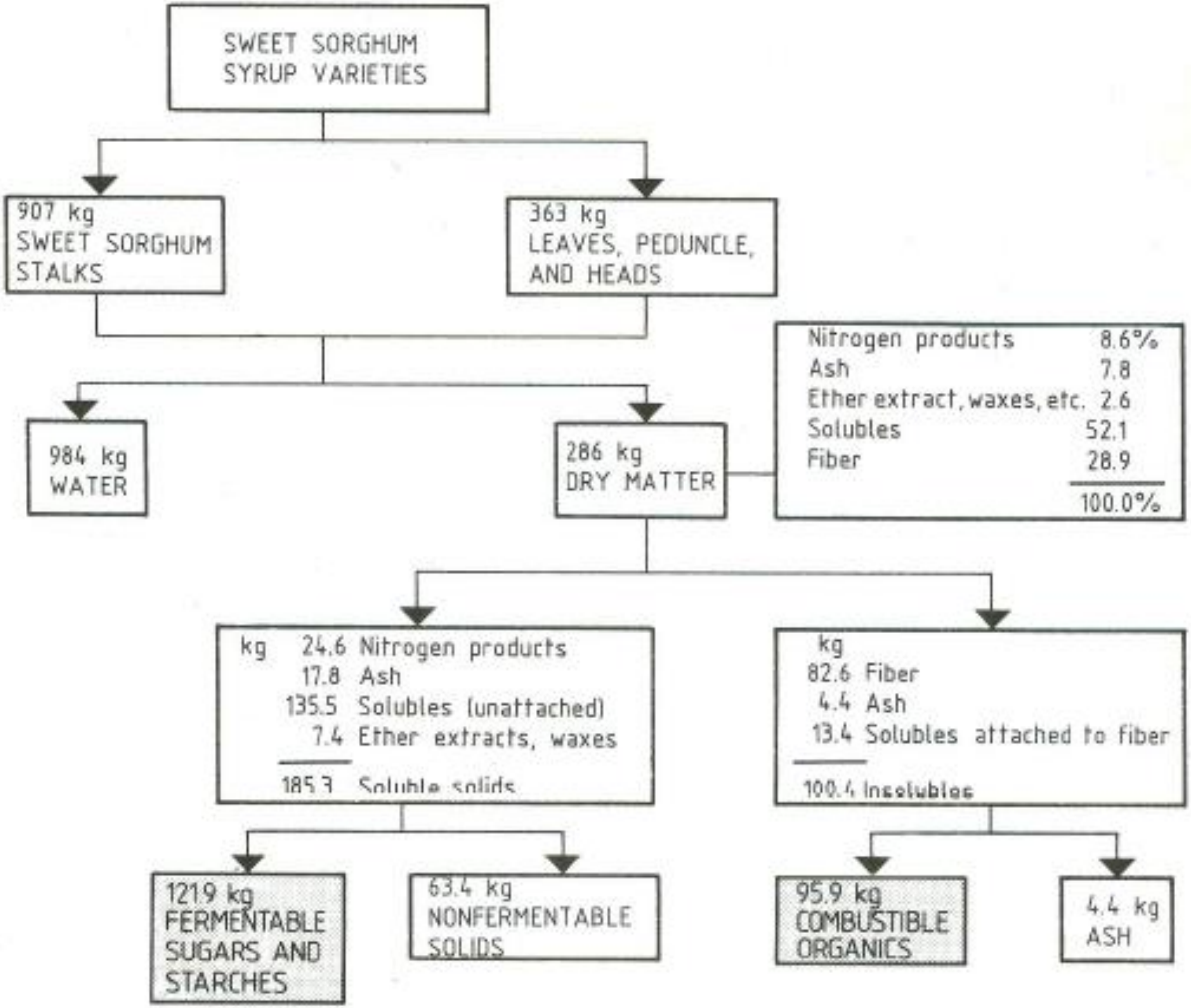
Figure 10. Flowsheet for commercial ethanol tower fermentation system (APV Co. Ltd.-system). Source: GREENSHIELDS and SMITH (1974). – FC flow controller, YCV yeast centrifugation vessel.

Table 10. Distribution of U.S. Corn Crop (Crop Year Ending Sept. 30, 1979) – Source: U.S. Dept. of Agriculture

Use	Quantity (35.24 mil L)	% of Crop
Food	488	6.9
Alcohol (includes beer)	69	1.0
Seed	18	0.3
Feed	4198	59.2
Export	2133	30.1
Total	6906	97.5

Table 11. Composition of Bitter Cultivars of Cassava – Source: DE MENEZES et al. (1978)

Component	g/100 g Dry Matter
Starch	80–89
Total sugars	3.6–6.2
Reducing sugar	0.1–2.8
Pentosans	0.1–1.1
Fiber	1.7–3.8
Protein	2.1–6.2
Fat	0.2–0.7
Ash	0.9–2.4



SWEET SORGHUM SYRUP VARIETIES
907 kg SWEET SORGHUM STALKS
363 kg LEAVES, PEDUNCLE, AND HEADS
984 kg WATER
286 kg DRY MATTER
Nitrogen products 8.6%
Ash 7.8
Ether extract, waxes, etc. 2.6
Solubles 52.1
Fiber 28.9
100.0%
kg 24.6 Nitrogen products
17.8 Ash
135.5 Solubles (unattached)
7.4 Ether extracts, waxes
185.3 Soluble solids
kg
82.6 Fiber
4.4 Ash
13.4 Solubles attached to fiber
100.4 Insolubles
121.9 kg FERMENTABLE SUGARS AND STARCHES
63.4 kg NONFERMENTABLE SOLIDS
95.9 kg COMBUSTIBLE ORGANICS
4.4 kg ASH

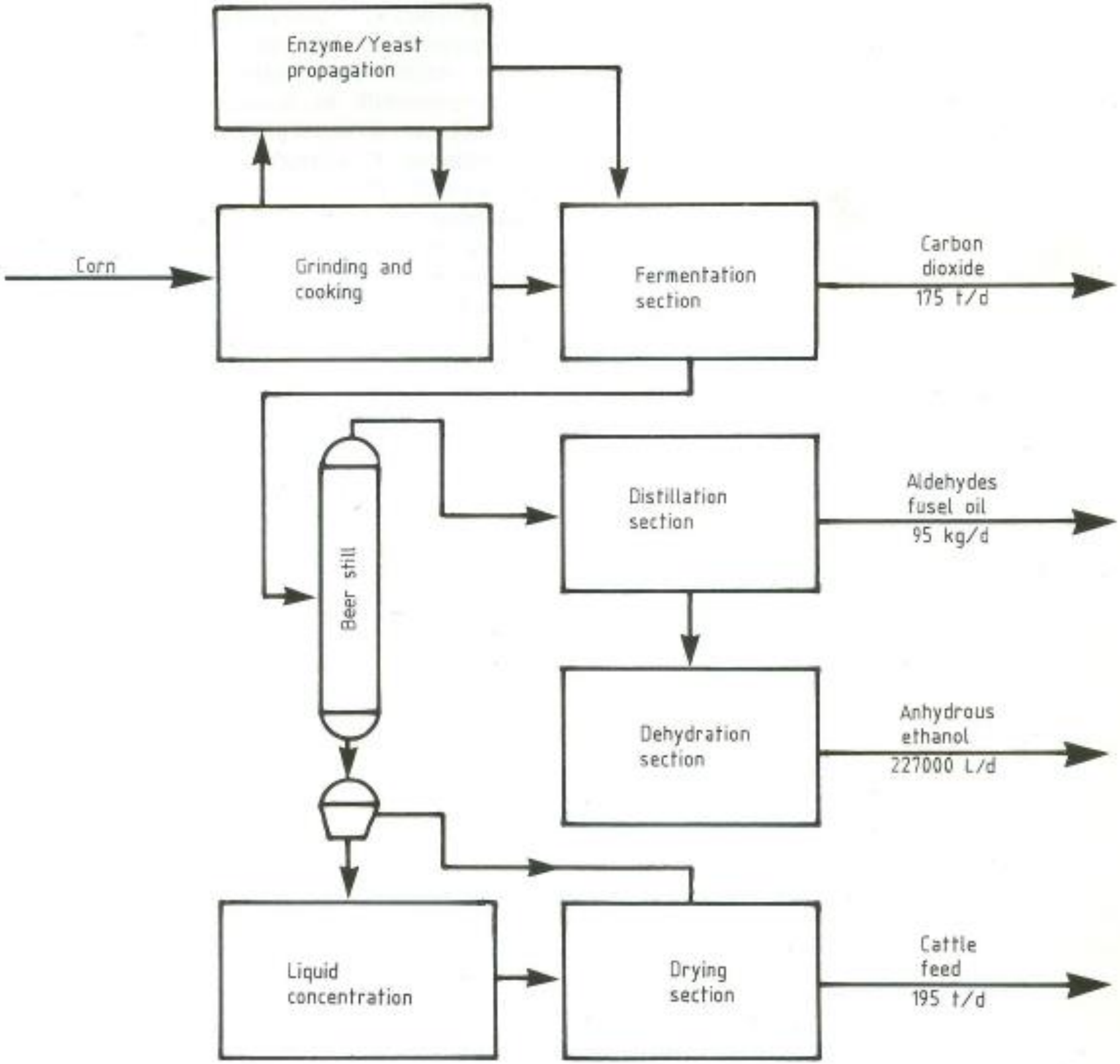


Figure 13. Proposed flow diagram for a conventional fermentation plant producing 76 million liters of anhydrous ethanol per year from corn. Source: SCHELLER (1976).

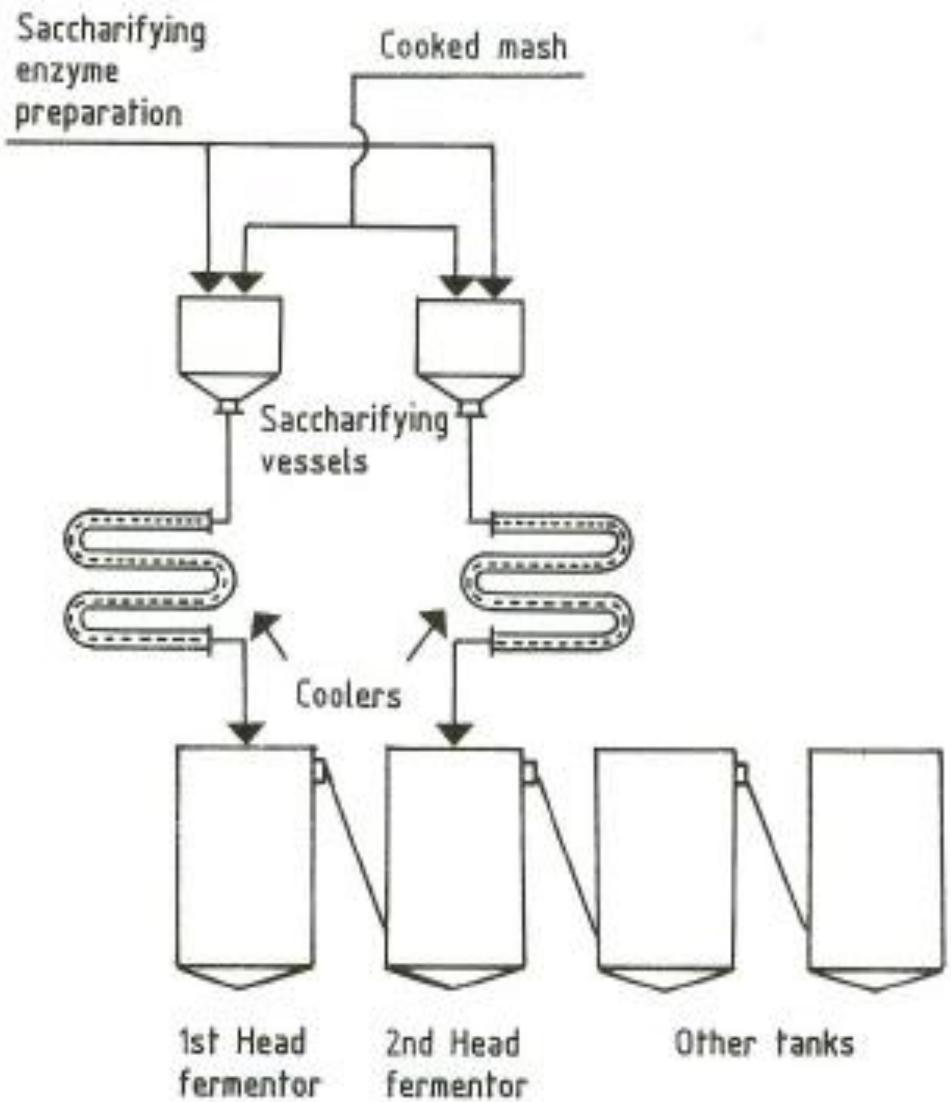


Figure 15. Simplified flowsheet for dual-flow mash saccharification system and multistage continuous alcoholic fermentation. Source: YAROVENKO (1978).

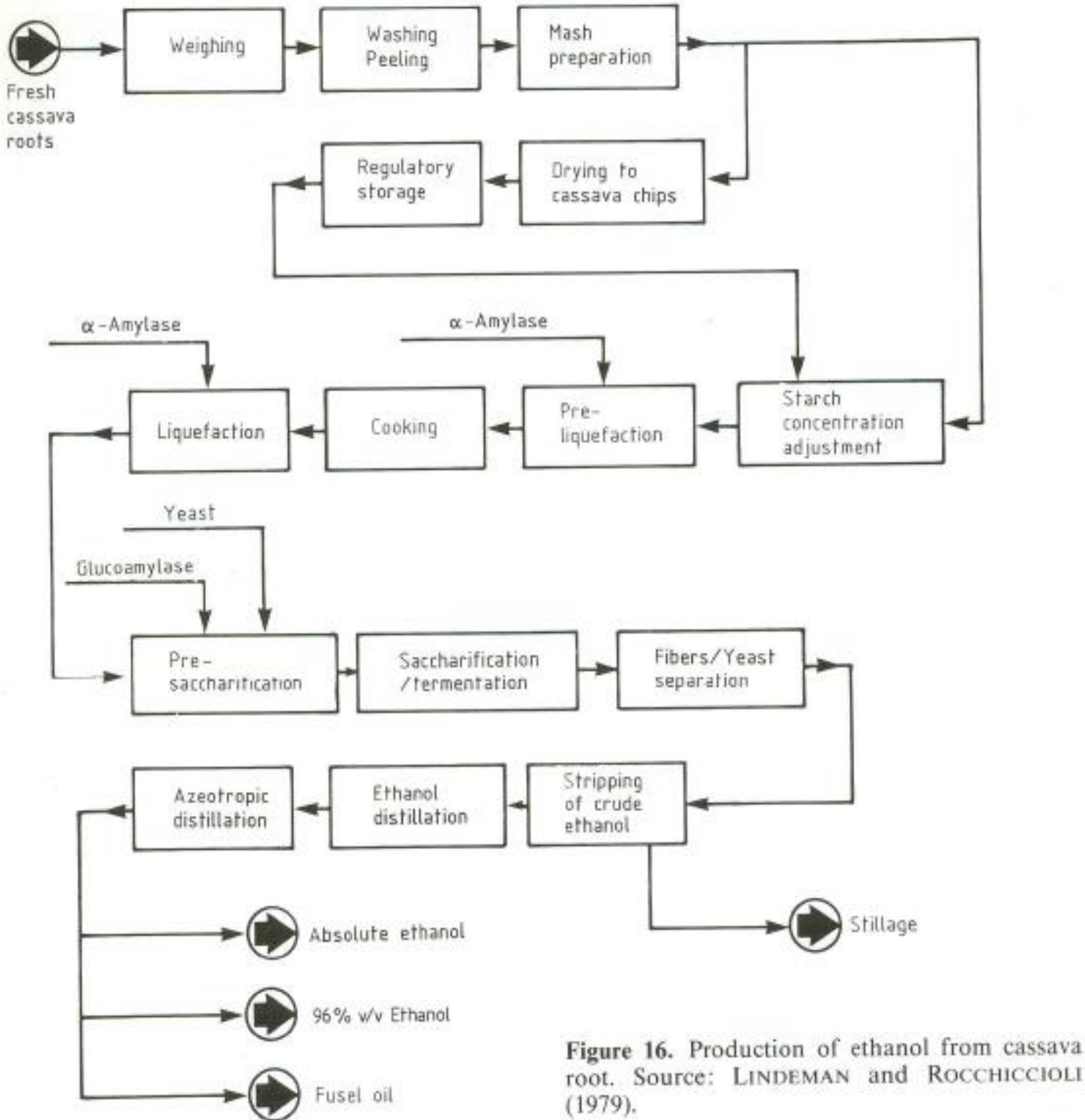


Figure 16. Production of ethanol from cassava root. Source: LINDEMAN and ROCCHICCIOLI (1979).

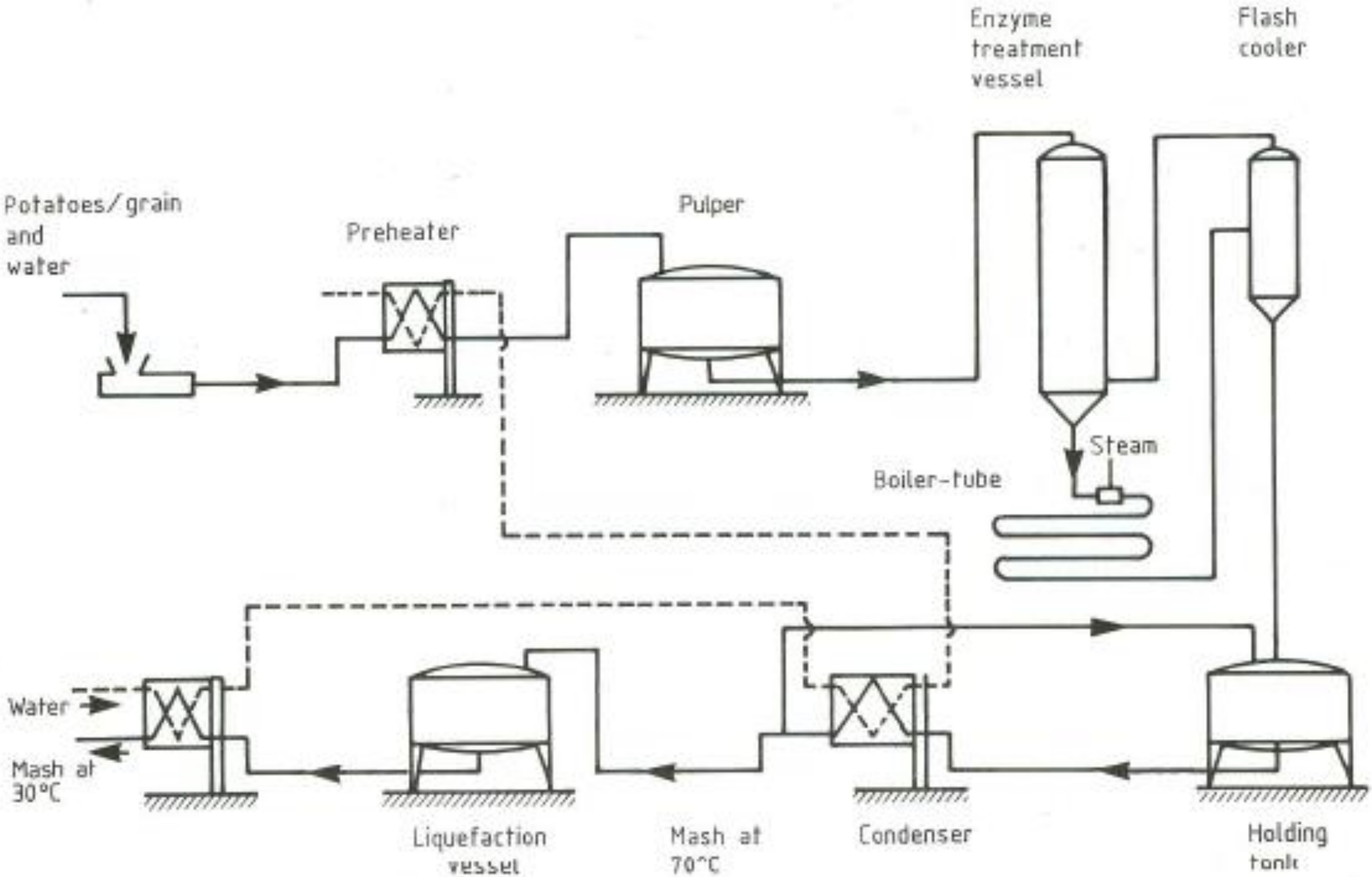


Figure 17. Danish Distilleries Ltd.'s semicontinuous production of alcohol from potatoes/grains. Source: ROSEN (1978).

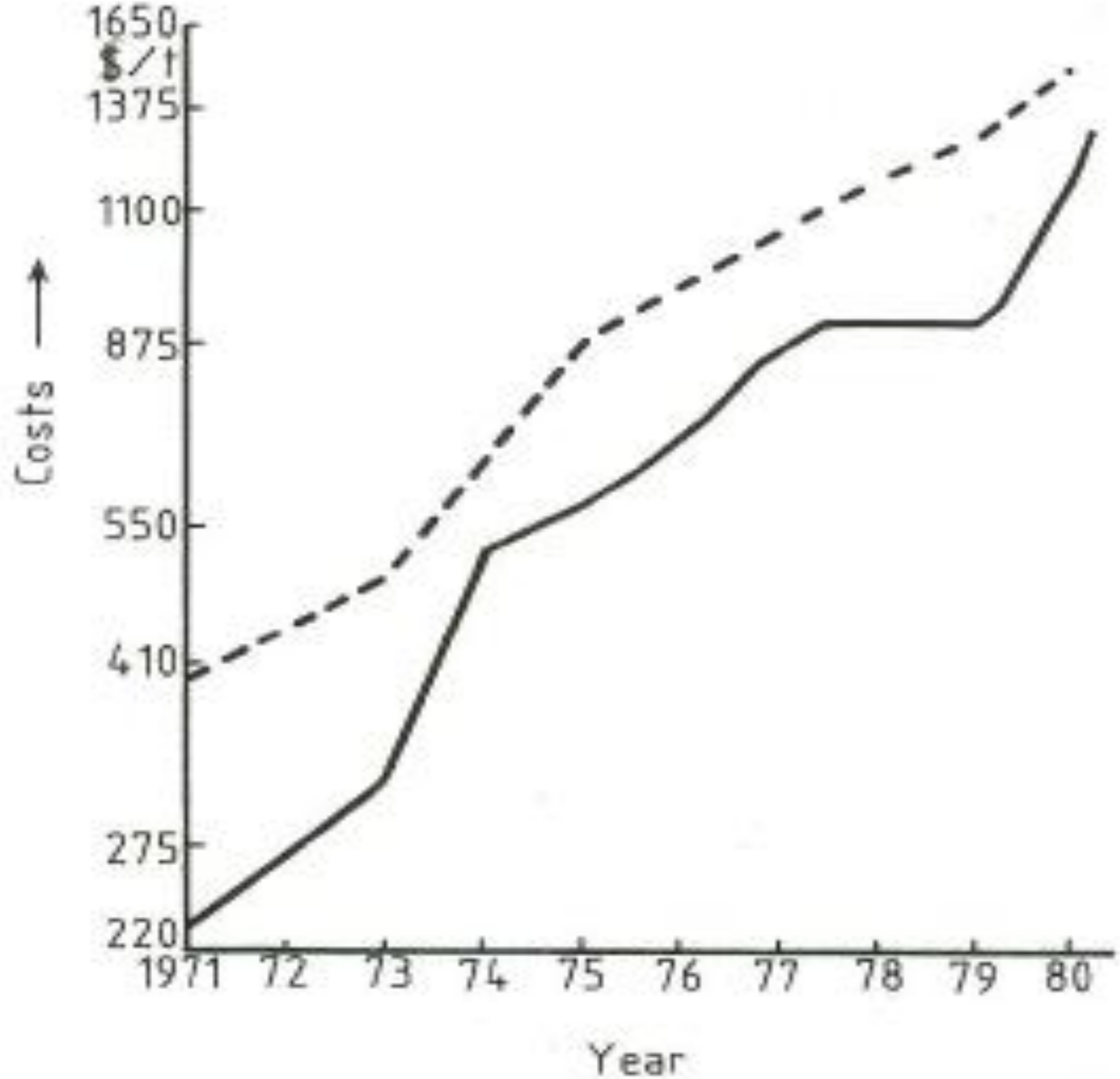


Figure 19. Comparison of ethanol production costs from cellulose with synthetic ethanol price. Source: VEAL and WHALLEY (1981). ---- cost of production from cellulose, ——— price of synthetic ethanol.

Table 12. Global Production of Representative Crops and Logging Residues on an Annual Basis and the Potential Glucose Yield From Each Type – Sources: GRETHLEIN (1978); KOSARIC et al. (1981); PIMENTEL et al. (1981); RIVERS and EMERT (1980); SITTON et al. (1979); THORNE and THORNE (1979)

Source	Global Production Area (10^3 ha)	Global Production Mass (10^3 t)	Residue Yield (t/ha)	Global Residue Production (10^3 t)	Composition of Residue			Potential Glucose Yield (10^3 t)
					Hexosan	Pentosan	Lignin	
Wheat	224111	363945	3.0	672333	31–51	23–38	18–21	208420–342890
Rice	137395	329358	7.4	1016700	32–53	21–24	12–25	325340–538850
Corn	112346	311030	5.6	629140	35	15	15	220200
Sugarcane	11667	57850	1.8	21000	45–55	25–27	19–21	9450–11550
Oats	32250	54374	4.0	129000	33.7	29.5	13.5	43473
Logging and Wood Processing (U.S. only)	—	—	—	53000	25	50	25	13250

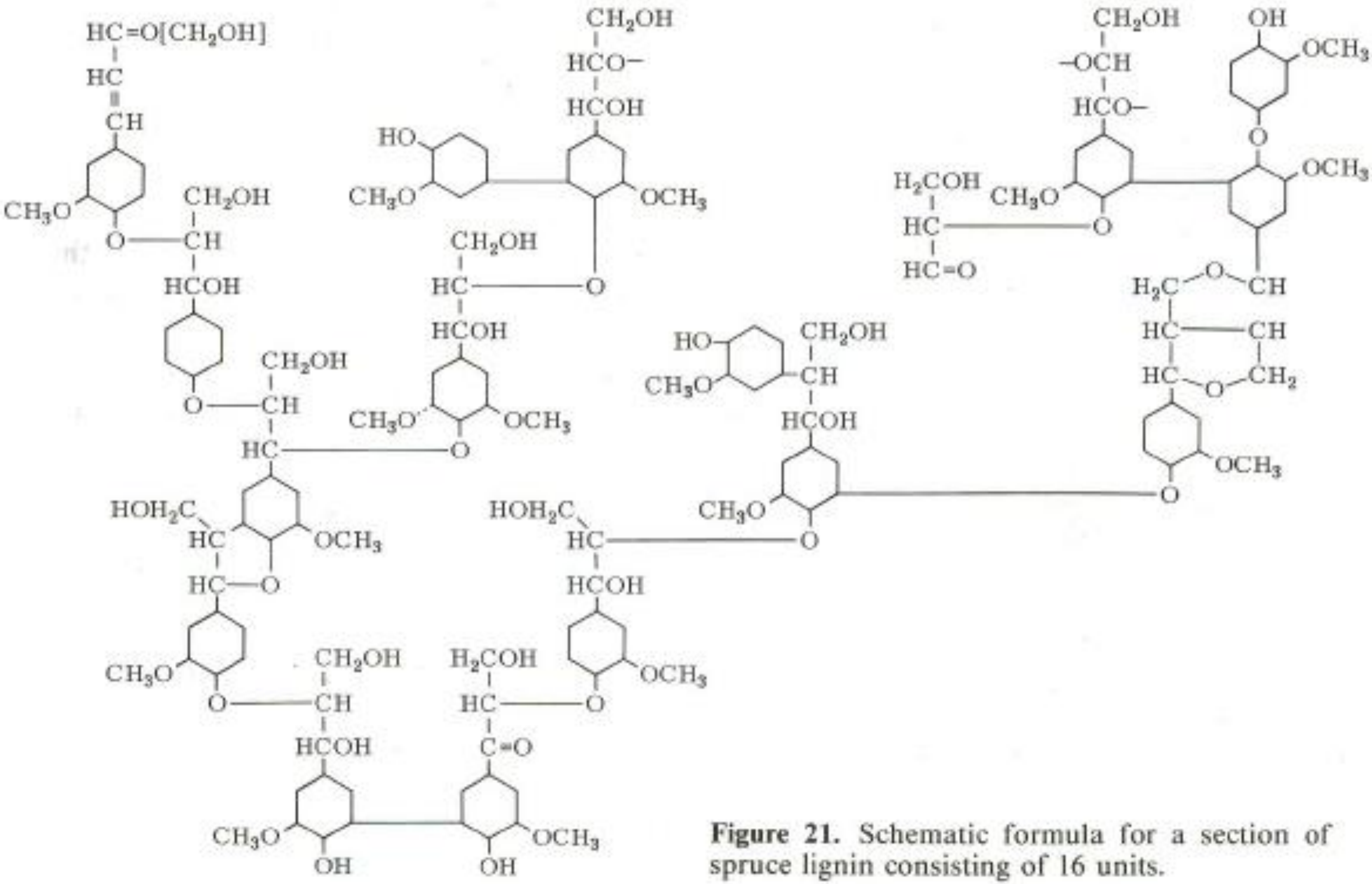


Figure 21. Schematic formula for a section of spruce lignin consisting of 16 units.

Table 14. Effect of Compression Milling Pretreatment on the Enzymatic Hydrolysis[a] of Various Cellulosic Substrates – Source: SPANO et al. (1979)

Substrate	Milling Time (min)	Total Reducing Sugars (mg/mL) 4 h	Total Reducing Sugars (mg/mL) 24 h
"Pure" celluloses			
Solka Floc (sw40)	0	10.5	16.8
	3	28.5	48.1
Absorbent cotton	0	2.5	3.9
	4	5.7	36.3
Wastes			
urban waste (B. Mines[b]) (w/o plastics)	0	10.7	18.5
	1.5	20.0	30.5
Xylitol process	0	3.5	6.7
	4	28.0	35.5
Softwoods			
Eastern spruce	0	2.0	3.8
	4	14.8	22.4
Western hemlock	0	1.2	2.0
	4	15.0	19.5
Hardwoods			
Maple	0	1.2	1.6
	5	21.8	28.6
Birch	0	1.6	2.4
	4	21.4	25.2
Agricultural residues			
Corn stover	0	4.6	8.0
	4	20.0	26.5
Sugarcane bagasse	0	1.6	2.5
	4	13.2	19.6

[a] *Trichoderma reesei* cellulase (QM9414), 19 IU/g substrate, 5% substrate slurries, pH 4.8, 50°C
[b] Municipal trash cellulose recovered by Bureau

Figure 23. Comparison of shake-flask and attrition methods for enzymatic hydrolysis of Whatmann CF-11 cellulose. Source: NEILSON et al. (1982). – △ Unmilled control, ○ ball milled, □ 60 g of glass beads, ● 136 g of stainless-steel beads, all with a shaker speed of 200 rpm (revolutions per minute), ◇ attrition at 200 rpm. PP 158: 1 IU/mL and 2% substrate. (IU international units for enzyme activity as described in text.)

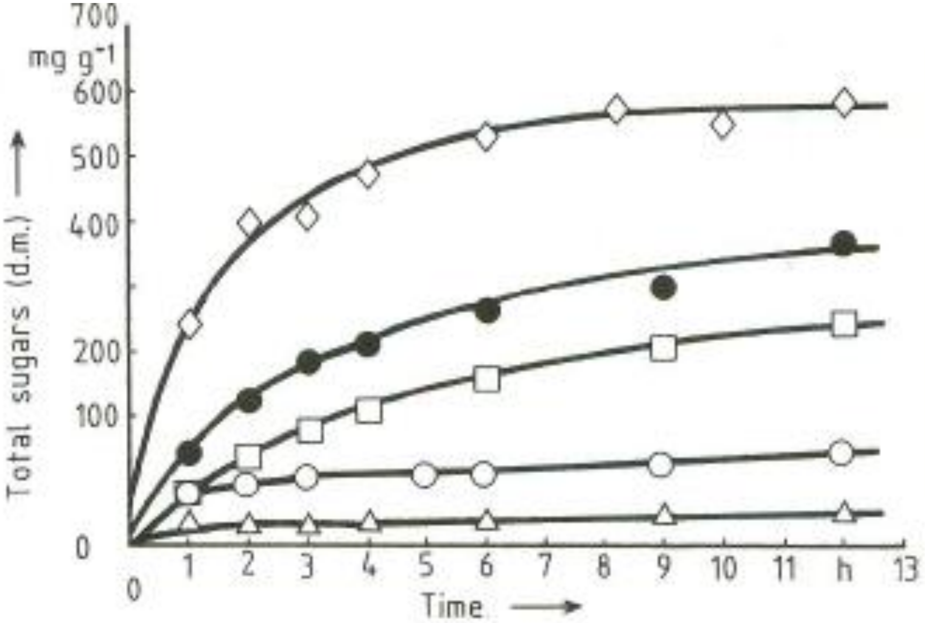


Table 15. Effect of Steam Pretreatment on the Enzymatic Hydrolysis[a] of Various Cellulosic Substrates – Source: SPANO et al. (1979)

Substrate	Pre-treatment	Total Reducing Sugars (mg/mL) 4 h	24 h
Hardwoods			
Poplar	None	1.4	2.4
	Steam	15.3	25.8
Aspen	None	1.8	3.0
	Steam	12.8	24.8
Agriculture residues			
Corn stover	None	4.9	7.8
	Steam	15.7	22.5
Sugar cane bagasse	None	1.7	2.5
	Steam	9.5	16.1
Urban waste	None	10.5	18.0
	Steam	6.2	10.8
Softwoods			
Eastern spruce	None	2.0	3.8
	Steam	3.5	6.4
Douglas fir	None	1.6	3.2
	Steam	2.8	4.3

[a] *Trichoderma reesei* cellulase (QM9414), 19 IU/g substrate, 5% substrate slurries, pH 4.8, 50°C, steamed substrates washed prior to enzymatic hydrolysis

Table 16. Examples of Microorganisms Capable of Degrading Lignin – Source: BISARIA and GHOSE (1981)

Fungi	Bacteria
Paecilomyces sp.	*Nocardia* sp.
Allescheria sp.	*Streptomyces* sp.
Preussia sp.	*Pseudomonas* sp.
Chaetomium sp.	*Flavobacterium* sp.
Poria sp.	

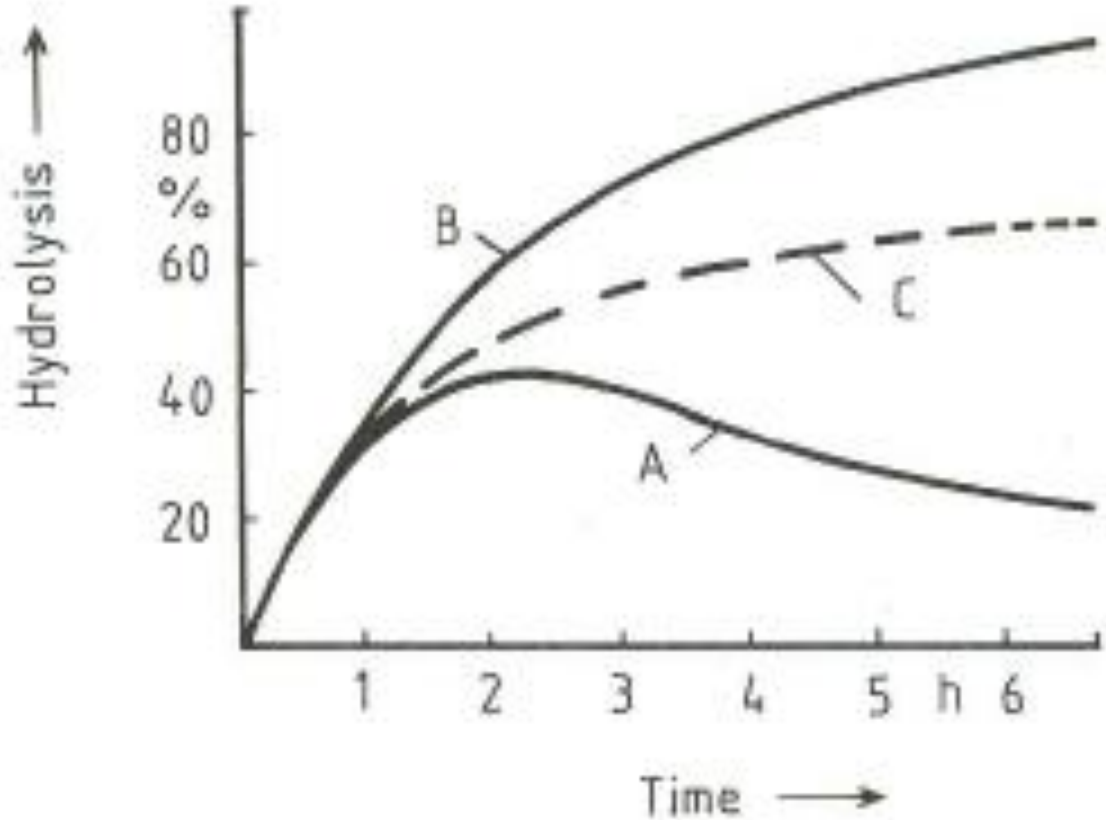


Figure 25. Formation of glucose by the dilute acid hydrolysis of cellulose. Source: WETTSTEIN and DEVOS (1980). – A: hydrolysis kinetics according to SAEMAN, B: ideal hydrolysis kinetics (no degradation), C: real hydrolysis kinetics.

BIBLIOGRAFIA

Kosaric, N. Ethanol- Potencial Source of Energy and Chemical Products. In *Biotechnology,* 2nd ed.:Rehm et al. VCH, Weinheim, 1996, Vol. 6, p.121-203.