QFL4520 – Química Ambiental II

Parte II – Recursos Naturais

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Última Atualização: 13/09/2017

Parte II – Recursos Naturais: Energia e Água

- *Energia - produção e usos;*
- *Combustíveis fósseis;*
- *Energia nuclear;*
- *Energia de fontes renováveis;*
- *Água – produção e uso.*

Aula 5:

- *Combustíveis fósseis;*

Combustíveis Fósseis

http://wiki.dickinson.edu/images/4/47/Coal-power-plant.jpg

Formação dos Combustíveis Fósseis

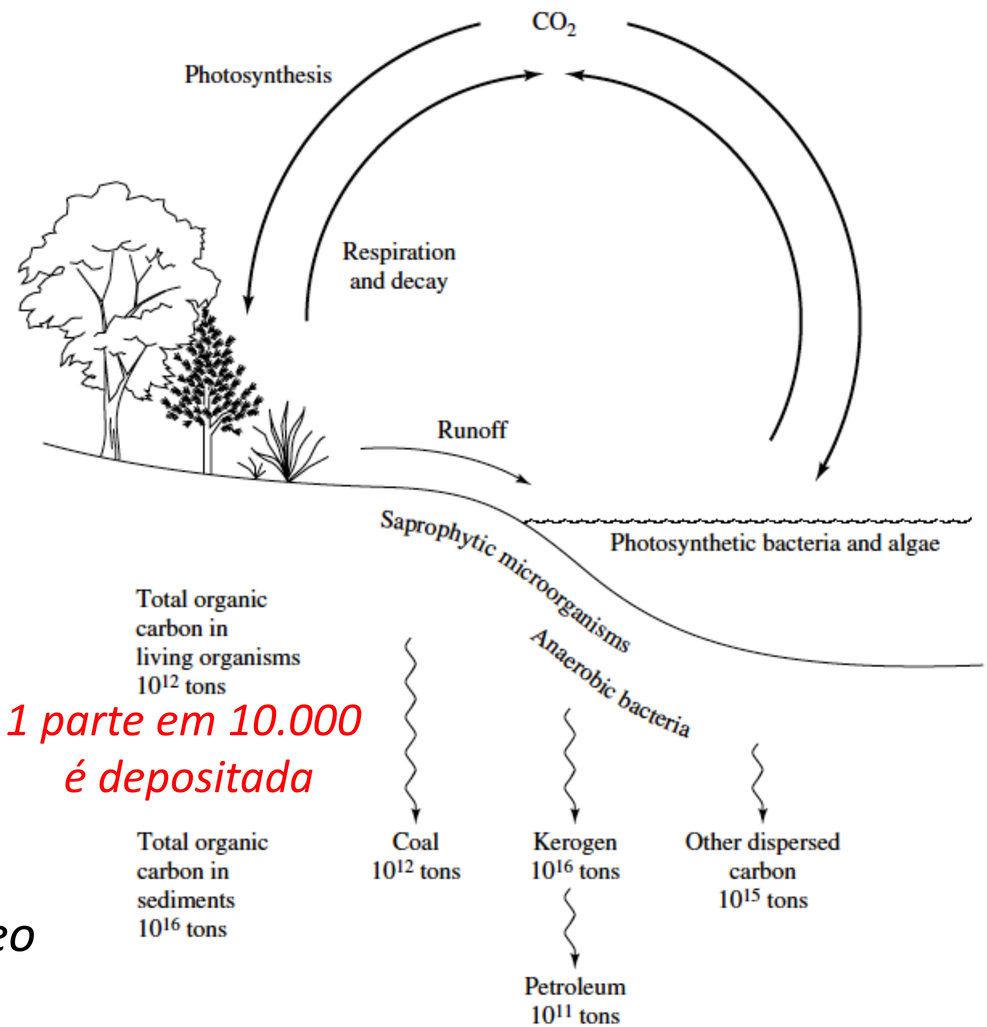
Fotossíntese

$$CO_2 + H_2O \overset{h\nu}{\rightarrow} \{CH_2O\} + O_2(g)$$

Respiração

$$\{CH_2O\} + O_2(g) \rightarrow CO_2 + H_2O$$

Produtividade primária líquida:
Carboidratos produzidos - consumidos



1 parte em 10.000 é depositada

Figure 2.1 Burial of organic carbon in the formation of fossil fuels. *Source:* Adapted from G. Ourisson et al. (1984). The microbial origin of fossil fuels. *Scientific American* 251(2):44–51. Reprinted with permission from J. Kuhl.

"Carbono reduzido" acumulado forma carvão, gás natural e petróleo ao longo de muito tempo

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Formação do Petróleo e Gás Natural

Fotossíntese nos oceanos
25 a 50 bilhões ton/ano de ”carbono reduzido”

↓ *Pequena fração é incorporada ao sendimentos (sem oxigênio)*

Sendimentos cobertos por areia e argila
(camada orgânica compacta numa matriz rochosa porosa)

↓

Bactérias anaeróbias digerem o material
(removendo N e O)

↓

Aumento de P e T = rearranjos e liberação de Metano e Hidrocarbonetos leves

↓

Petróleo (na matriz porosa) / Metano (sob rocha impermeável)

Formação do Petróleo

Composto encontrado na membrana de bactérias

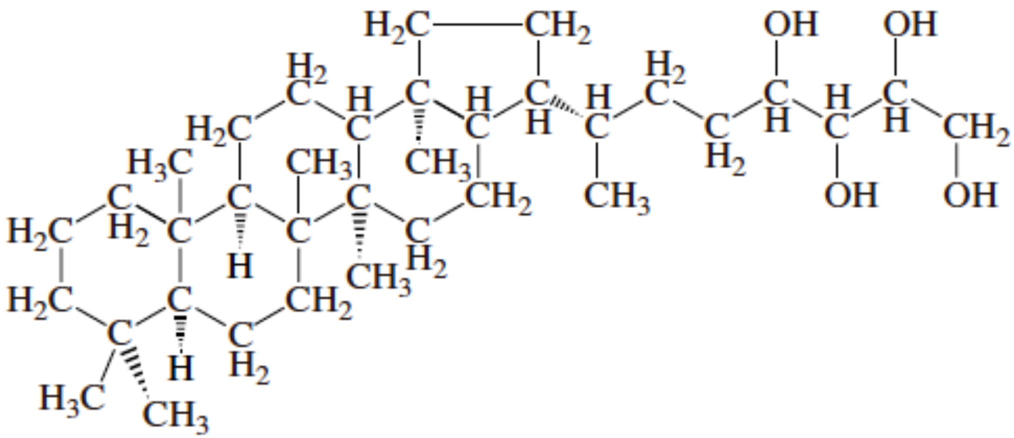
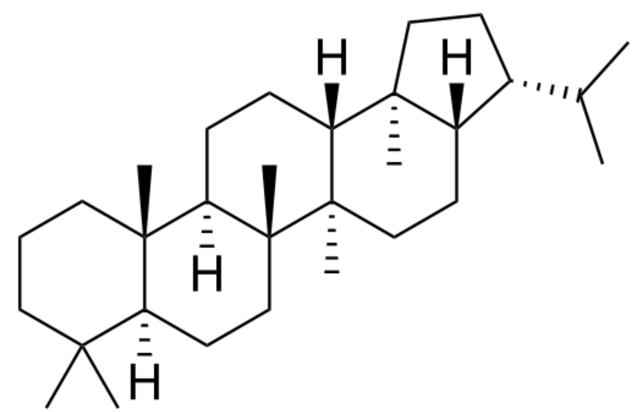


Figure 2.2 The structure of bacteriohopanetetrol.

Hopano, encontrado no petróleo



Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Formação do Petróleo

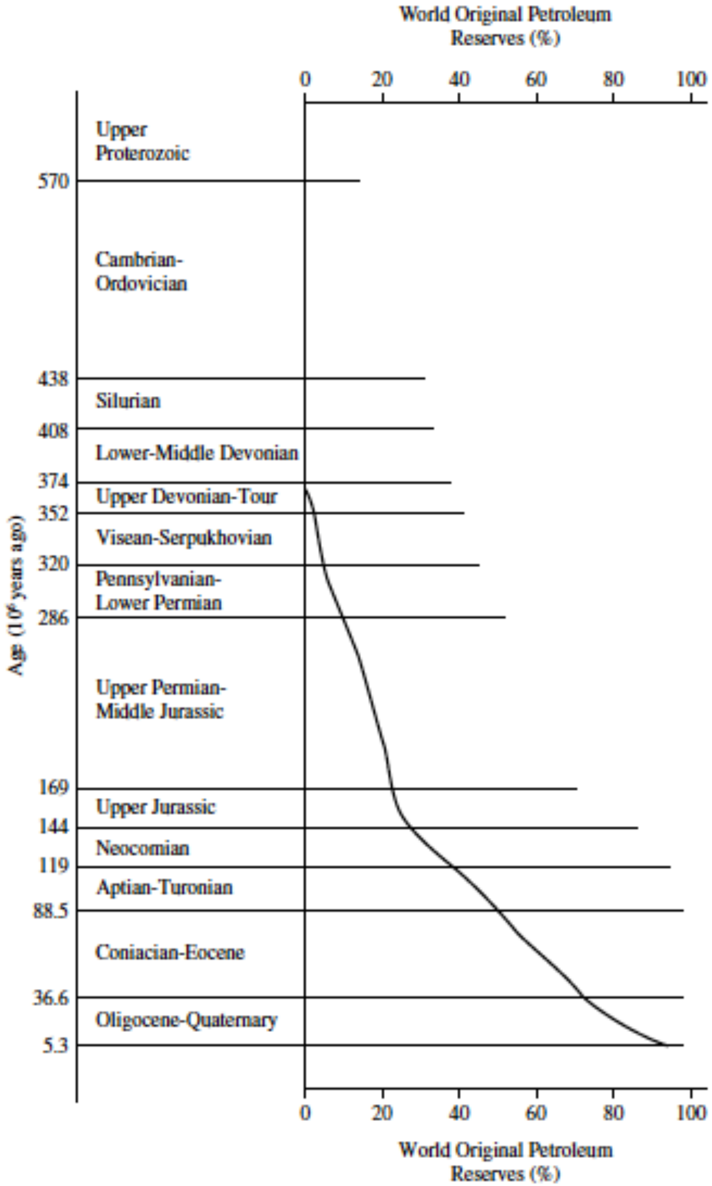
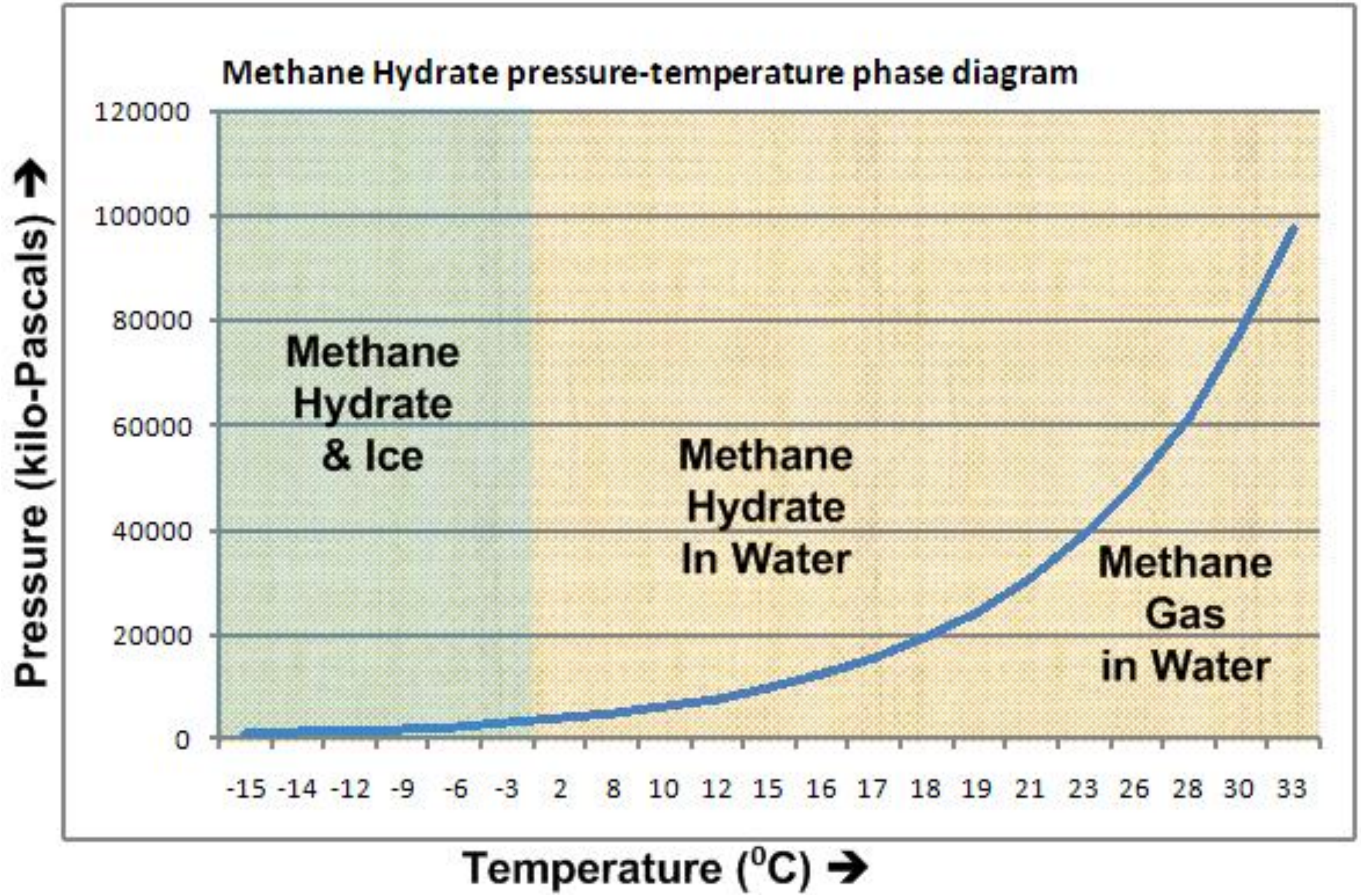


Figure 2.3 Cumulative chart of effective source rock deposition in the formation of petroleum. *Source:* Adapted from H.D. Klemme and G.F. Ulmishek (1991). Effective petroleum source rocks of the world: Stratigraphic distribution and controlling depositional factors. *The American Association of Petroleum Geologists Bulletin* 75:1809–1851. AAPG Copyright © 1991. Reprinted by permission of the AAPG whose permission is required for further use.

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Depósitos de clatratos de metano

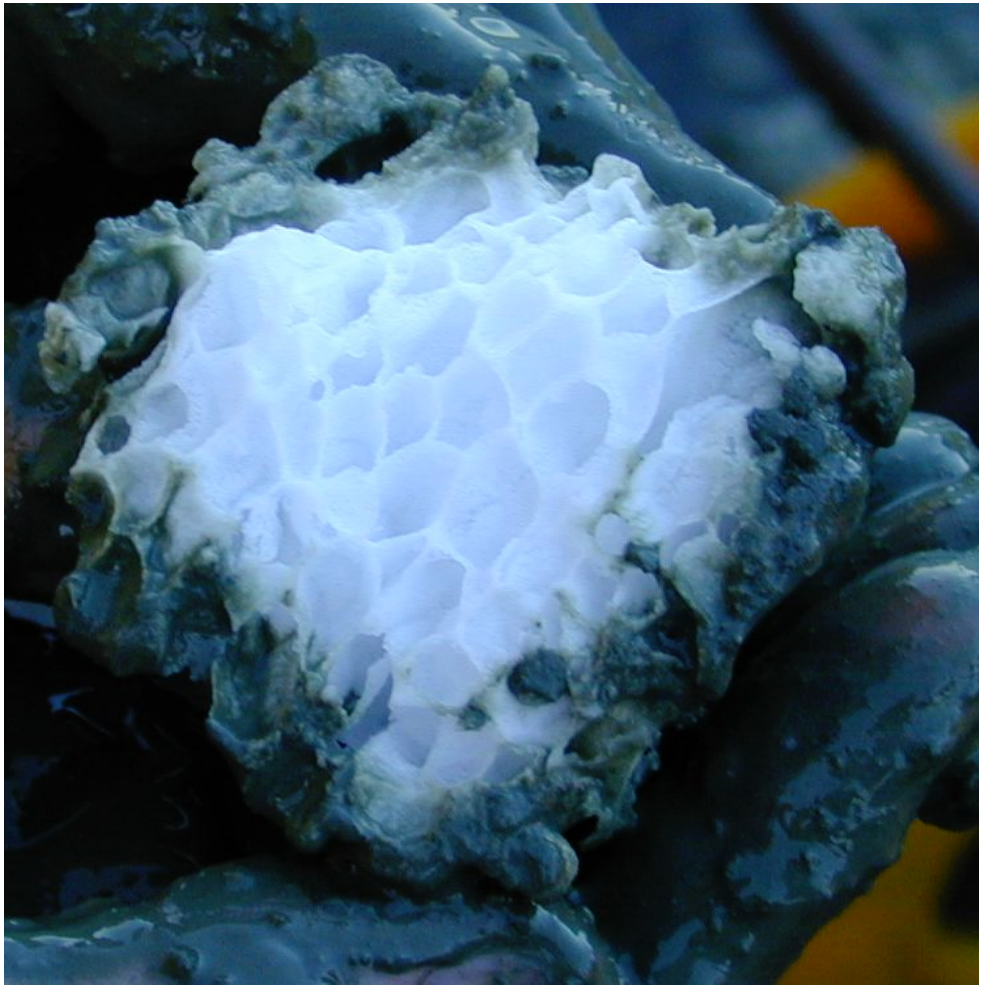
Diagrama de fases do metano em água



https://upload.wikimedia.org/wikipedia/commons/b/b4/Methane_Hydrate_phase_diagram.jpg

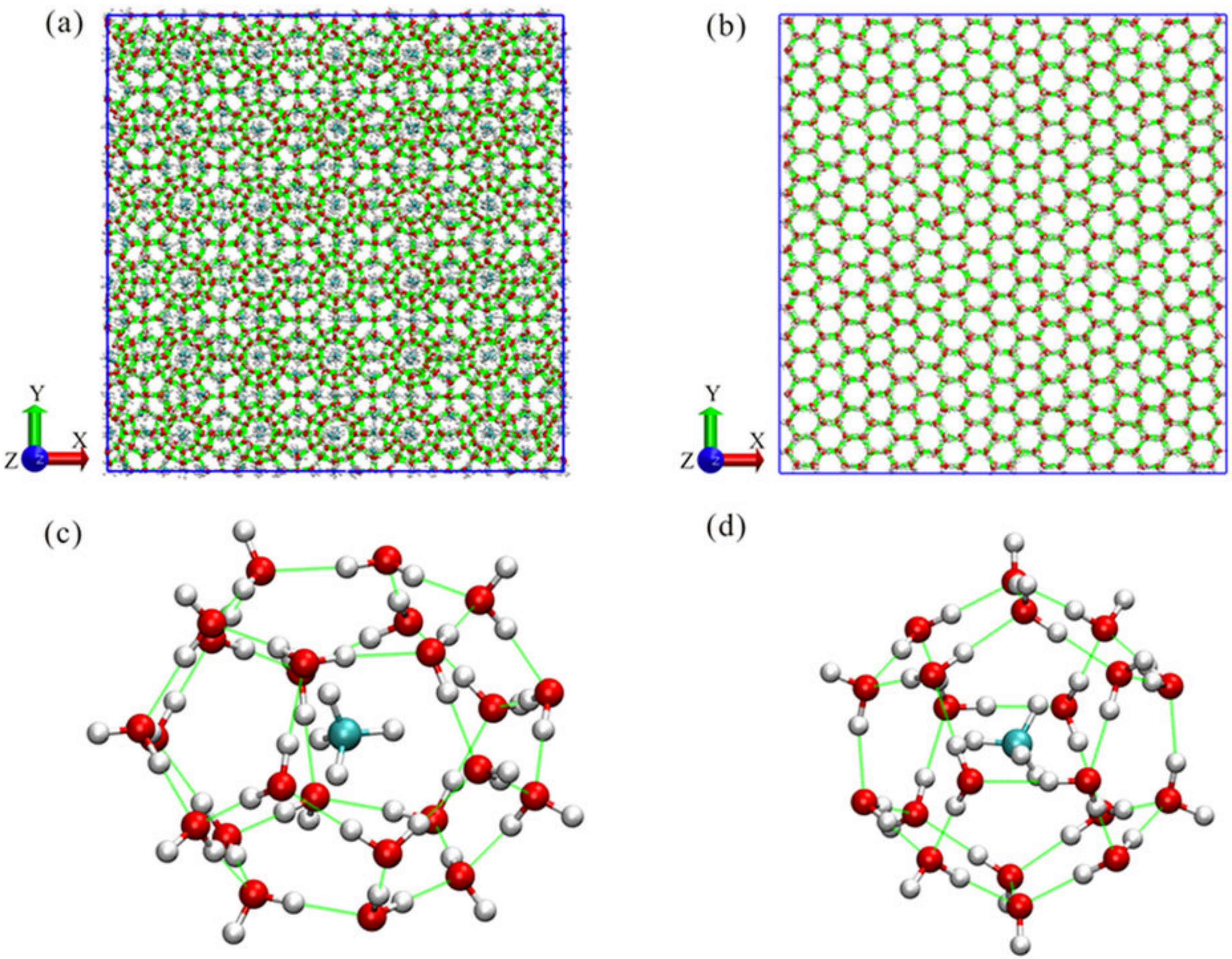
Clatratos de metano

Clatrato de metano encontrado no sedimento no fundo do mar
(Costa do Oregon – 1200 m de profundidade)



https://upload.wikimedia.org/wikipedia/commons/6/60/Gashydrat_mit_Struktur.jpg

Clatratos de metano



Molecular structures of (**a**) methane hydrate (sI) and (**b**) normal ice (Ih). (**c**) Large ($5^{12}6^{2}$) and (**d**) small (5^{12}) methane hydrate cages.

Scientific Reports 6, Article number: 23548 (2016) - doi:10.1038/srep23548

Formação do Carvão

Plantas "lenhosas" em pântanos (lignina + celulose)

↓ *Pequena fração é incorporada ao sendimentos (sem oxigênio)*

Bactérias aeróbias oxidam celulose mas não a lignina

↓

Compactação em camadas de turfa

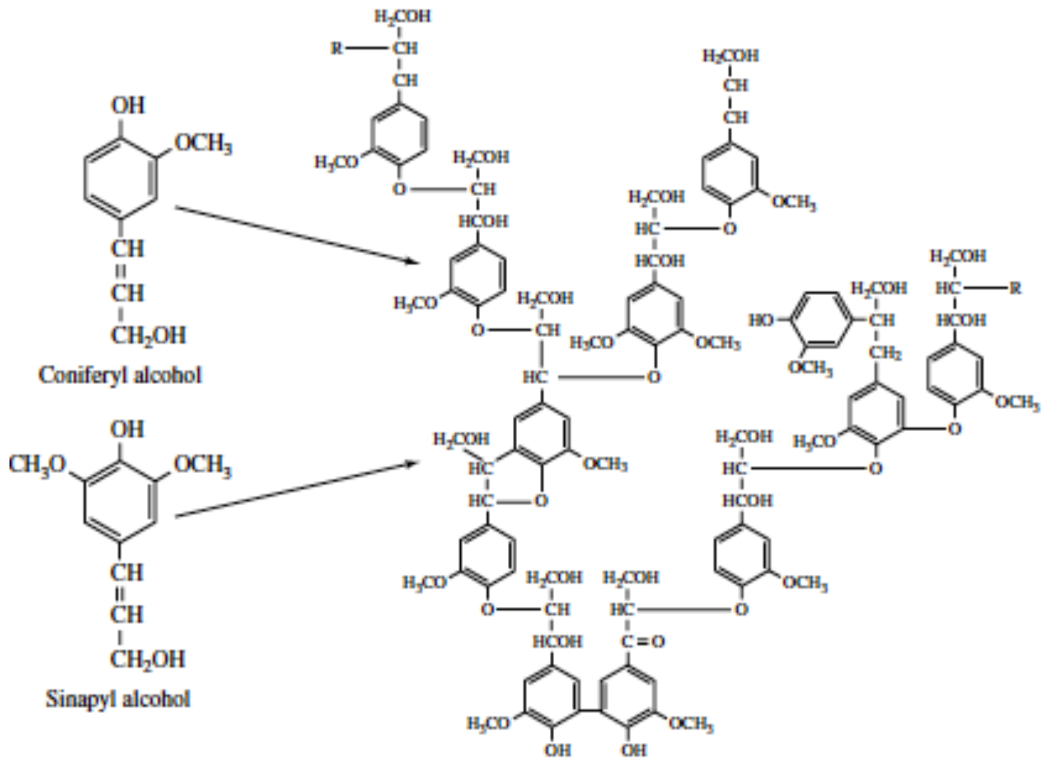
↓

Temperaturas e pressões altas ao longo de muito tempo

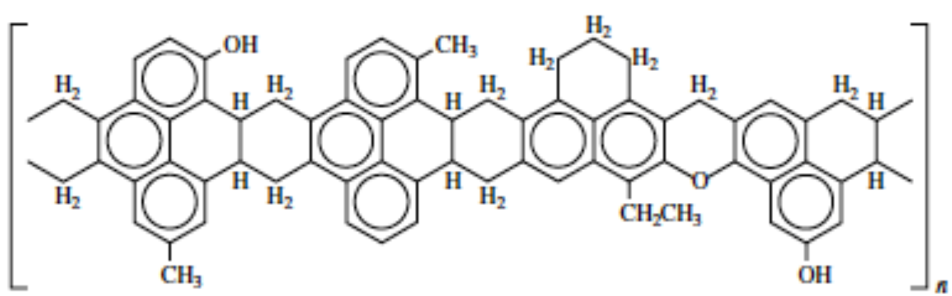
↓

Carvão

Formação de Carvão



Representative structure for a part of the lignin polymer



Representative structure of bituminous coal

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Energias de Combustão

TABLE 2.2 COMBUSTION ENERGETICS ESTIMATED FROM BOND ENERGIES

	Energy content (kJ)				
	Reaction enthalpy	Per mole O_2	Per mole fuel	Per gram fuel	Moles CO_2 per 1,000 kJ
Hydrogen: $2H_2 + O_2 = 2H_2O$	482	482	241	120	0
Gas: $CH_4 + 2O_2 = CO_2 + 2H_2O$	810	405	810	51.6	1.2
Petroleum: $2(—CH_2—) + 3O_2 = 2CO_2 + 2H_2O$	1,220	407	610	43.6	1.6
Coal: $4(—CH—) + 5O_2 = 4CO_2 + 2H_2O$	2,046	409	512	39.3	2.0
Ethanol: $C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O$	1,257	419	1,257	27.3	1.6
Cellulose: $(—CHOH—) + O_2 = CO_2 + H_2O$	447	447	447	14.9	2.2

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Petróleo

https://3c1703fe8d.site.internapcdn.net/newman/gfx/news/hires/2014/1-fournewmachi.jpg

Refino de Petróleo

Composição do Petróleo – Mistura complexa:

- Hidrocarbonetos (maior proporção);
- Enxofre (até 10%);
- Oxigênio (até 5%);
- Nitrogênio (até 1%);
- Traços de V, Ni, Fe, Al, Na, Ca, Cu e U.

Hidrocarbonetos no petróleo:

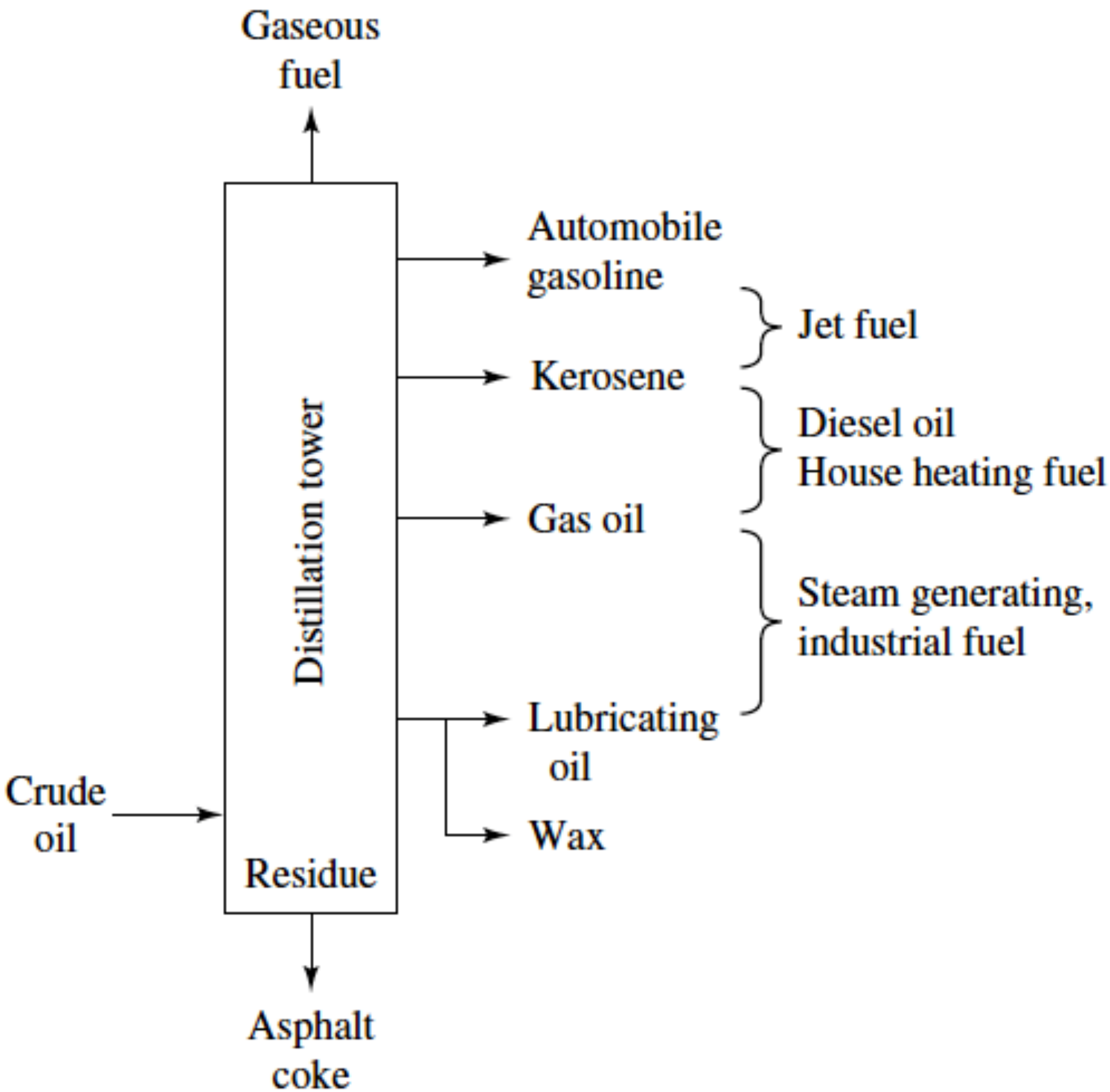
- Alifáticos/saturados (maioria);
- Aromáticos (até 10%).

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Refino do Petróleo

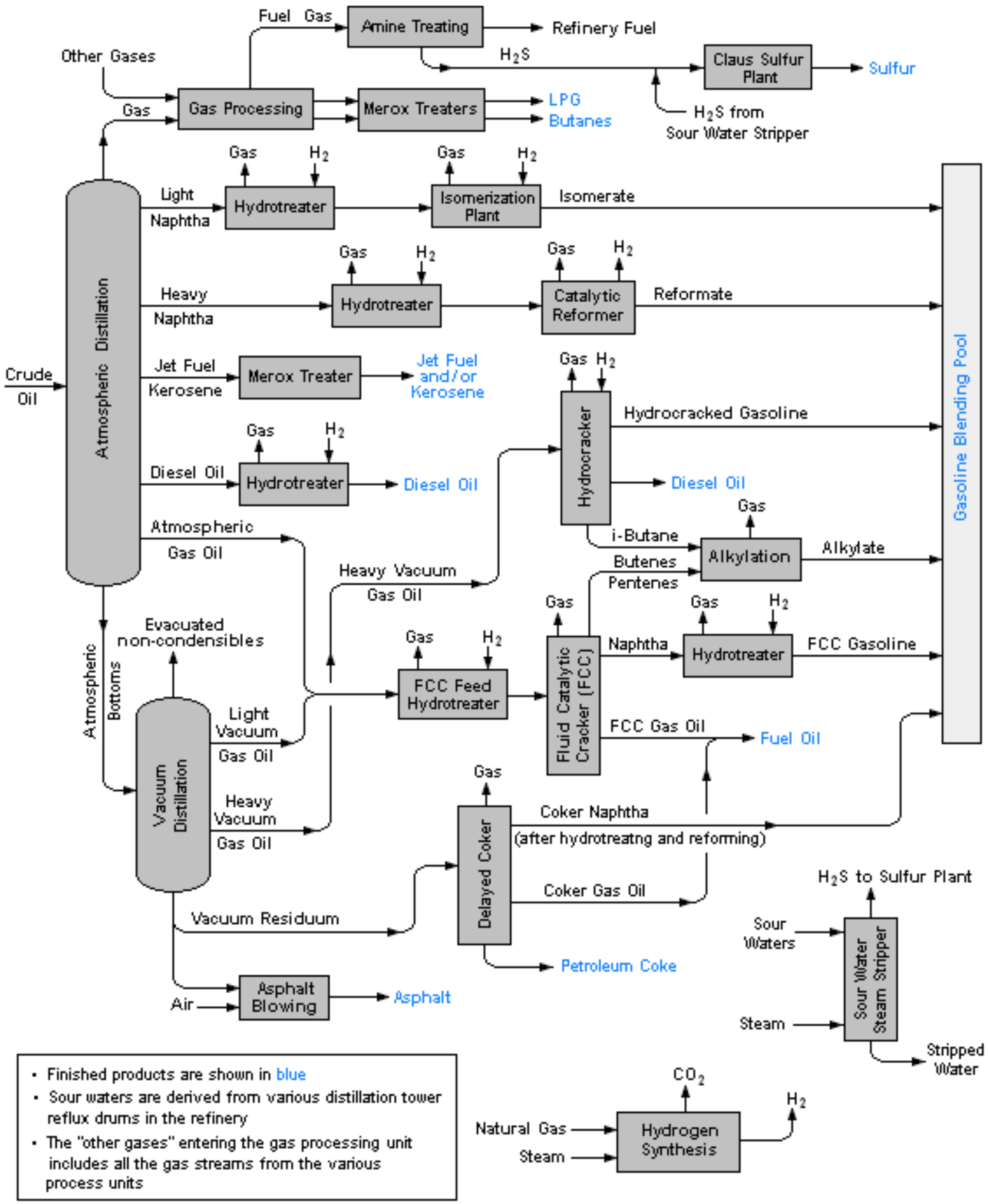
- Destilação;
- Transformação química;
- Tratamento.

Refino de Petróleo



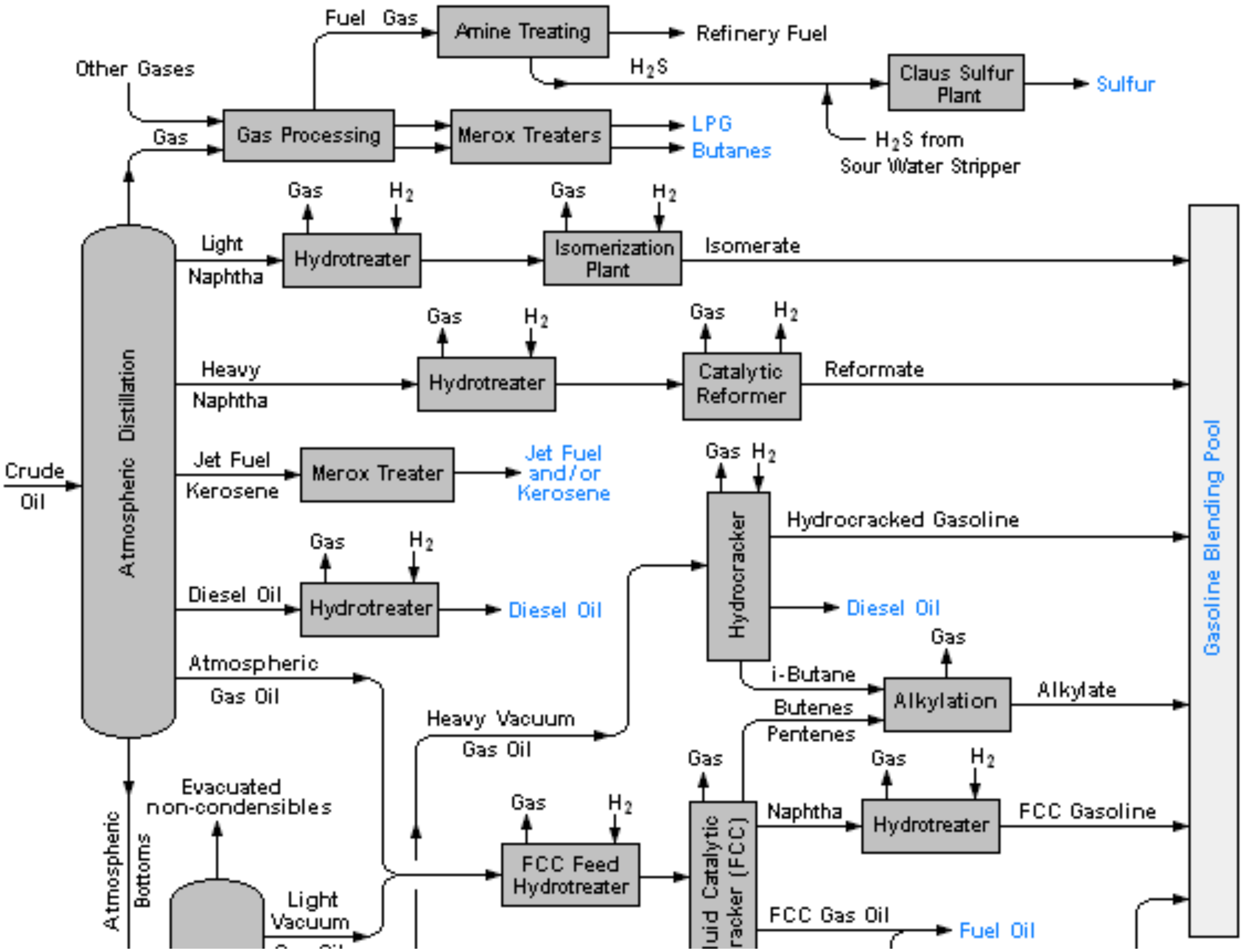
Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Refino de Petróleo



https://en.wikipedia.org/wiki/Oil_refinery #/media/File:RefineryFlow.png

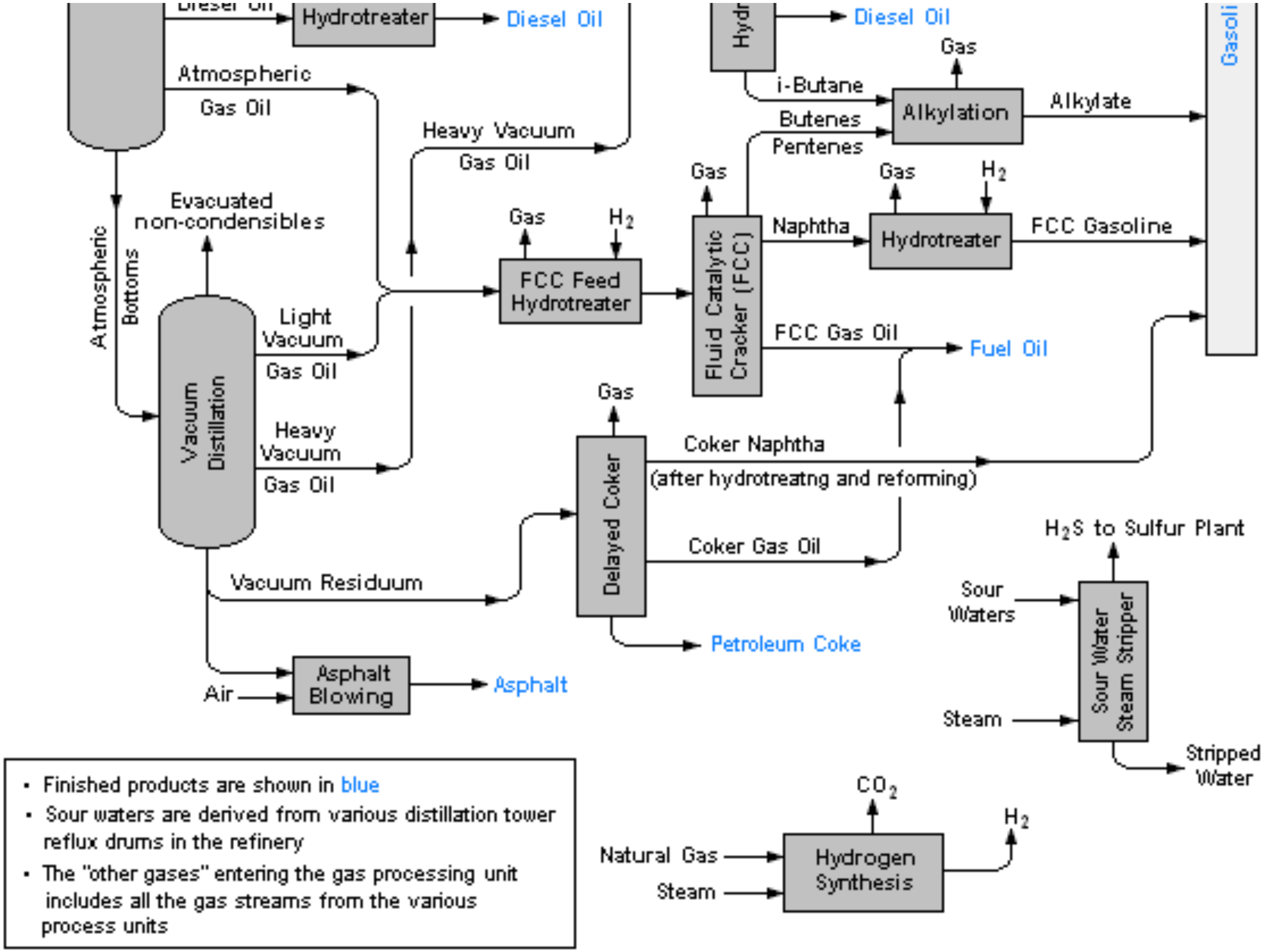
Refino de Petróleo



https://en.wikipedia.org/wiki/Oil_refinery#/media/File:RefineryFlow.png

Reinaldo C. Bazito

Refino de Petróleo



https://en.wikipedia.org/wiki/Oil_refinery#/media/File:RefineryFlow.png

Refino de Petróleo

Fraction	Chemical Composition		
	Carbon atoms	Molecular weight	Boiling range, °C
Gaseous	1–4	16–58	–126–0
Gasoline	5–12	72–170	0–204
Kerosene	10–16	156–226	180–274
Gas oil	15–22	212–294	260–371
Lube oil	19–35	268–492	338–468
Residue	36–90	492–1262	468+

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

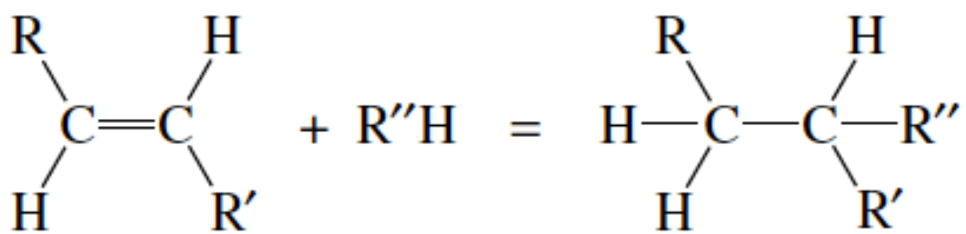
Refino de Petróleo

Craqueamento

$$C_{(m+n)}H_{2(m+n)+2} = C_mH_{2m} + C_nH_{2n+2}$$

alkane (kerosene or gas-oil size) — alkene — alkane (gasoline size)

Alquilação

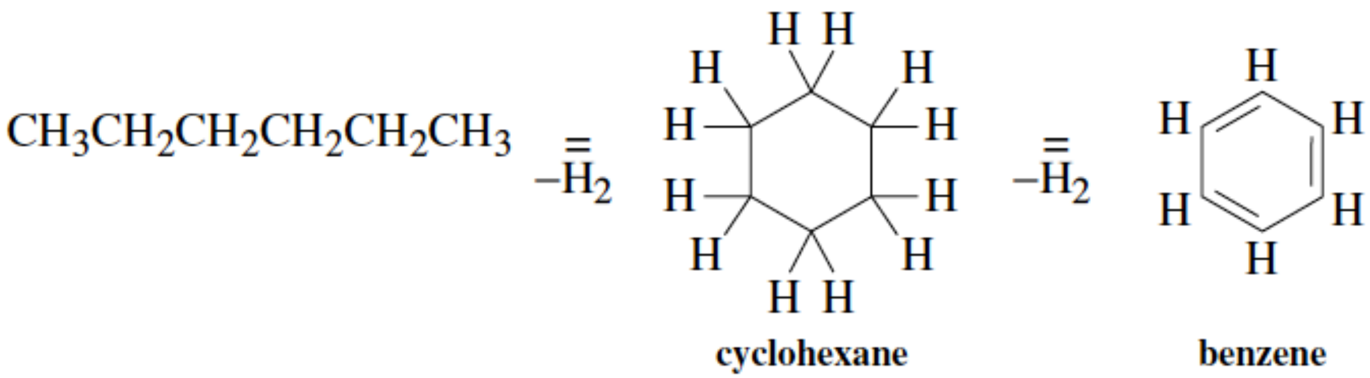


light hydrocarbons (3, 4, or 5 carbon atoms) — gasoline

Aumentam fração de gasolina de 20% em volume para 40-45% em volume

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Reforma catalítica



Aumento da ”octanagem”

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Petróleo

”Vantagens”:

- Líquido (facilidade de transporte);
- Relativamente limpos (hidrocarbonetos);
- Sistema integrado e eficiente de extração, transporte, refino e entrega final.

”Desvantagens”:

- Derrames de óleo cru ou derivados;
- Emissões.

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Rotas de transporte de petróleo

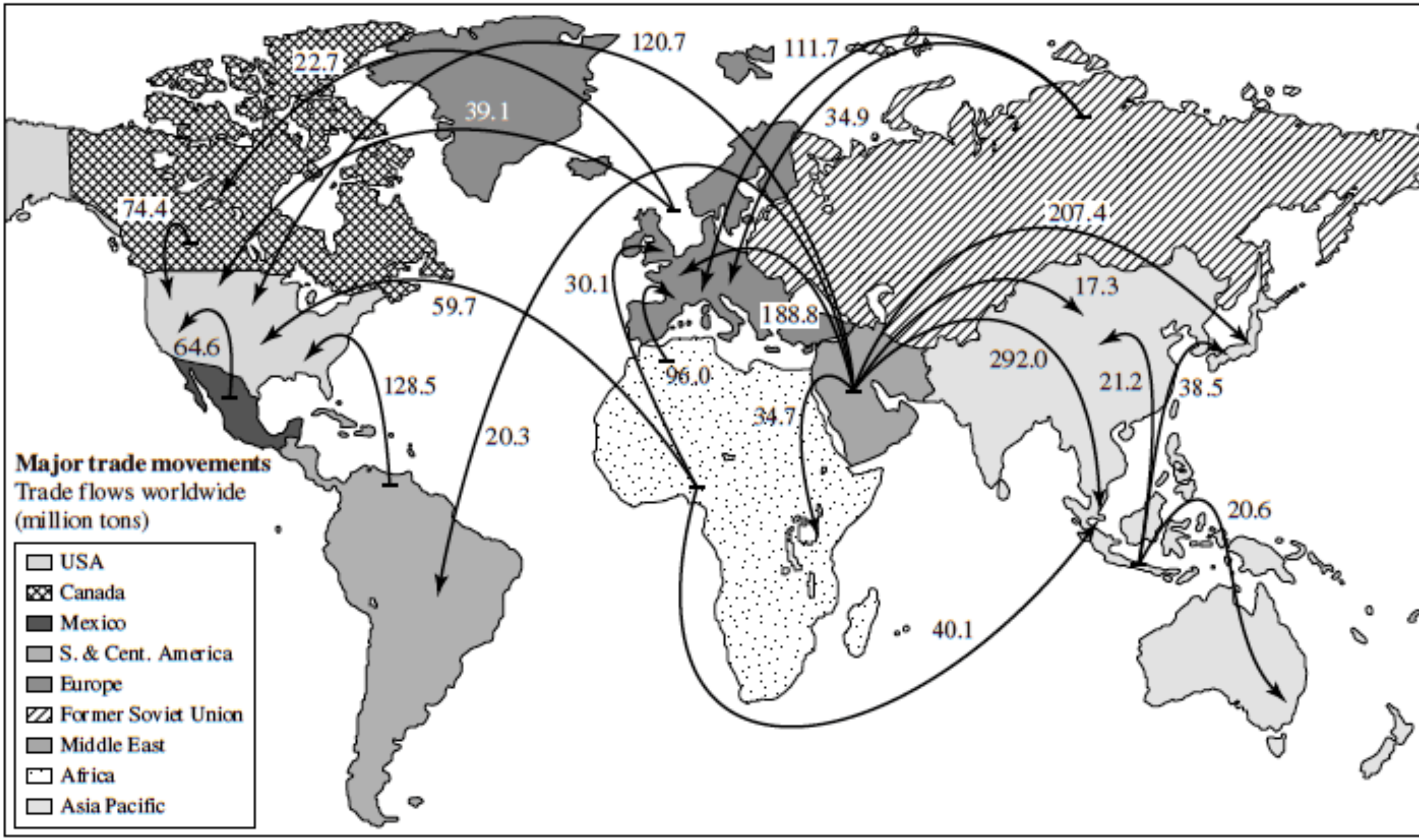


Figure 2.6 Routes of international oil trade. *Source:* BP Amoco, *Statistical Review of World Energy 2000*. (http://www.bp.com/centres/energy/world_stat_rev/oil/trade.asp)

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Derramamentos de Petróleo

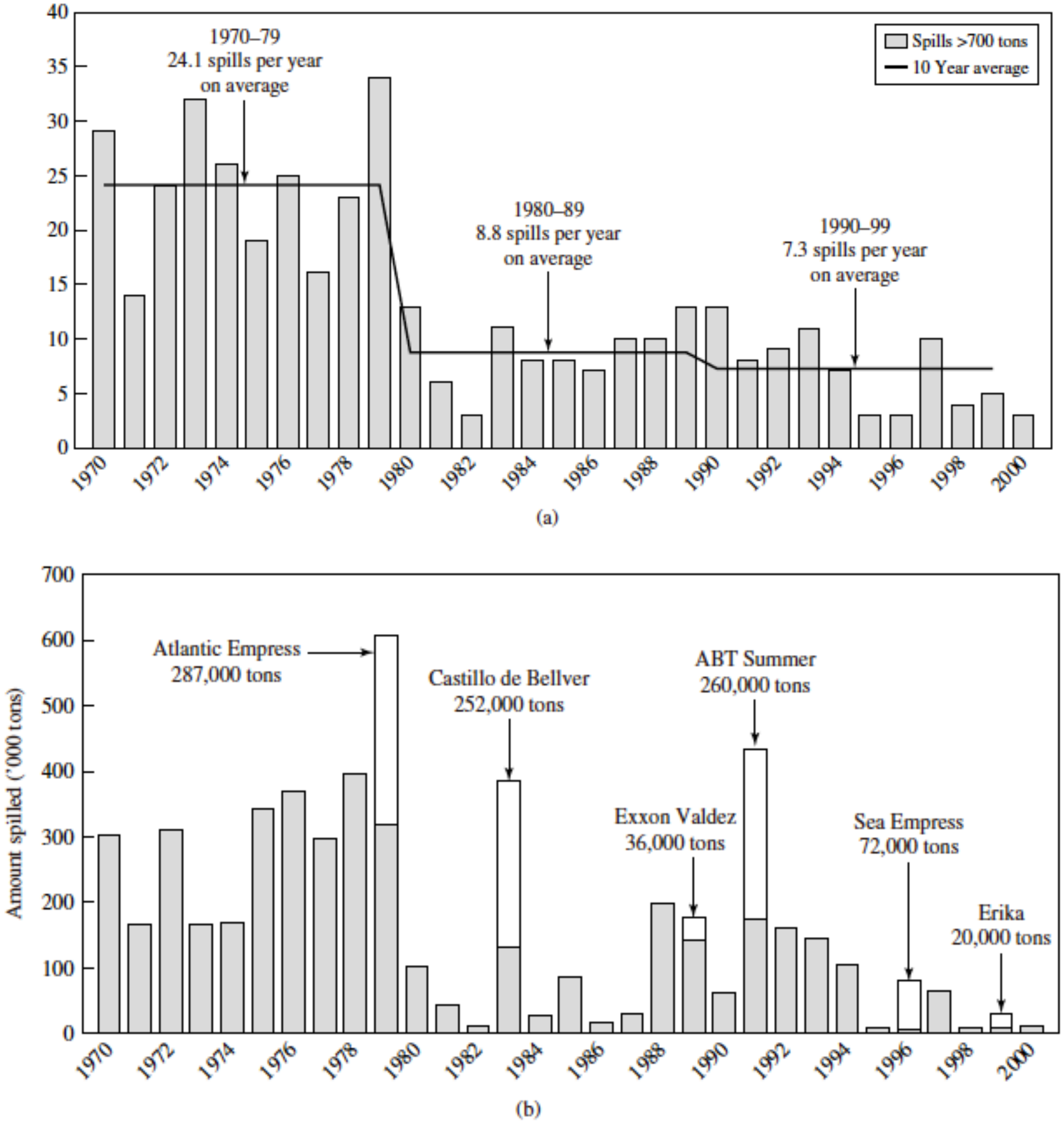


Figure 2.7 a) Trend in number of international oil spills; b) Trend in quantity of oil spills. White sections of bars indicate major tanker oil spills. *Source:* International Tanker Owners Pollution Federation. *Tanker Oil Spill Statistics* (2000). (http://www.itopf.com/stats/html)

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Derramamentos de Petróleo

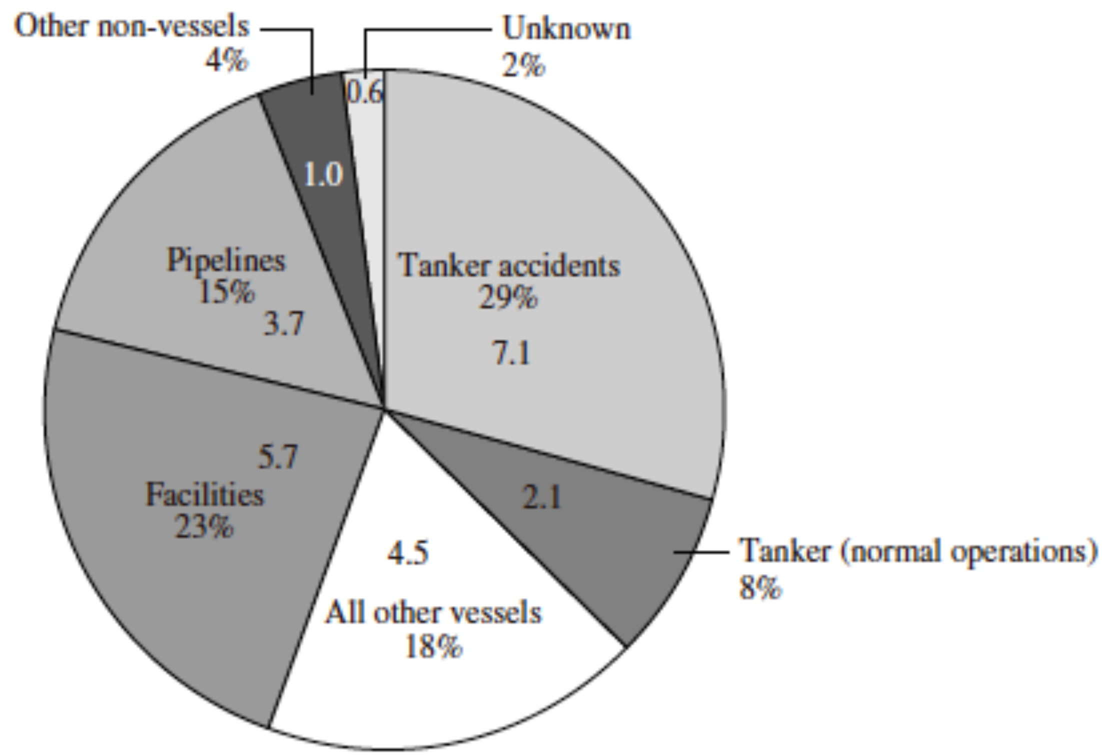


Figure 2.8 Sources of oil inputs to U.S. Waters, 1995–1999 (thousands of metric tons). *Source:* U.S. Coast Guard, *Polluting Incident Compendium, Cumulative Data and Graphics for Oil Spills, 1973–1999, Oil Spill Compendium Data Table, Volume of Spills by Source*. (http://www.uscg.mil/hq/g%2Dm/nmc/response/stats/C8Data.htm)

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Há fontes naturais de Petróleo no mar!

Figure 2.9 Locations of reported marine seeps. *Source:* National Research Council (1985). *Oil in the Sea* (Washington, DC: National Academy Press).

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Destino do Petróleo num derramamento no mar

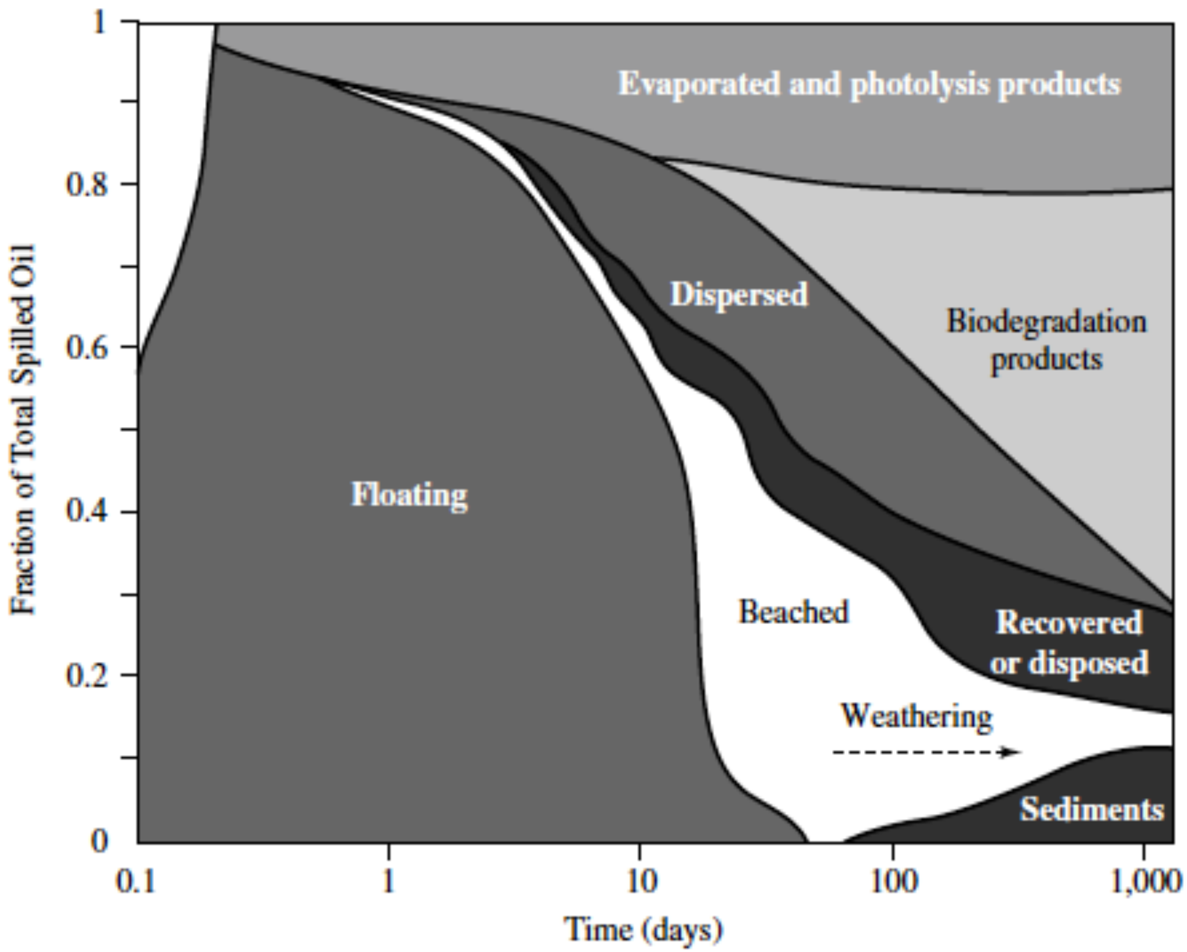


Figure 2.10 Overall fate of oil spilled in the *Exxon Valdez* accident over time period from March 1989 through Autumn 1992. *Source:* D.A. Wolfe et al. (1994). The fate of the oil spilled from the *Exxon Valdez*. *Environmental Science and Technology* 28:561A–568A. Reprinted with permission from ES&T. Copyright (1994) American Chemical Society.

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Emissões

- CO_2

TABLE 2.2 COMBUSTION ENERGETICS ESTIMATED FROM BOND ENERGIES

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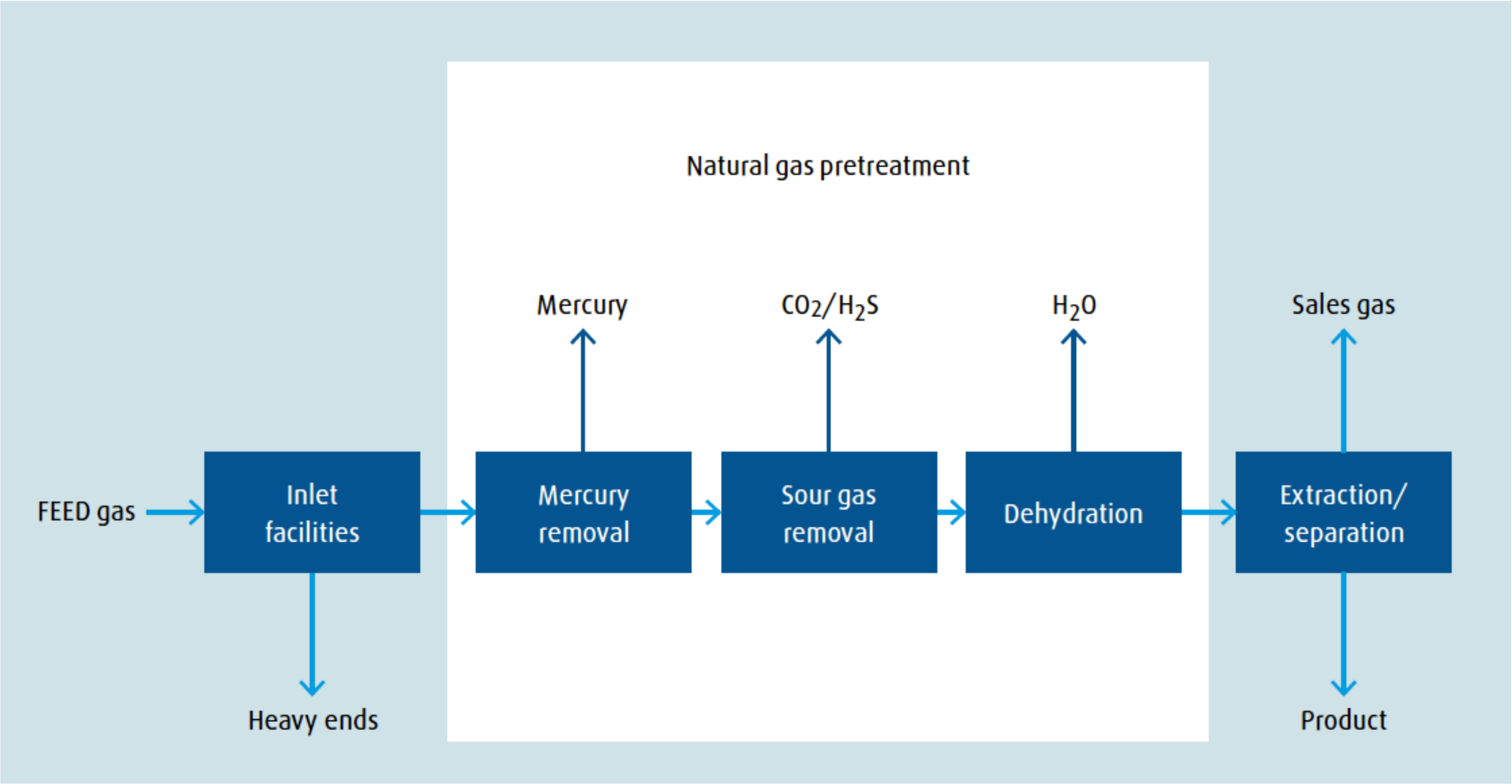
- CO e Hidrocarbonetos não queimados
- Material particulado (HPAs)
- NO_x

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Gás Natural

https://abrilexame.files.wordpress.com/2016/09/size_960_16_9_ax189_6a8a_966.jpg?quality=70&strip=info

Processamento de Gás Natural



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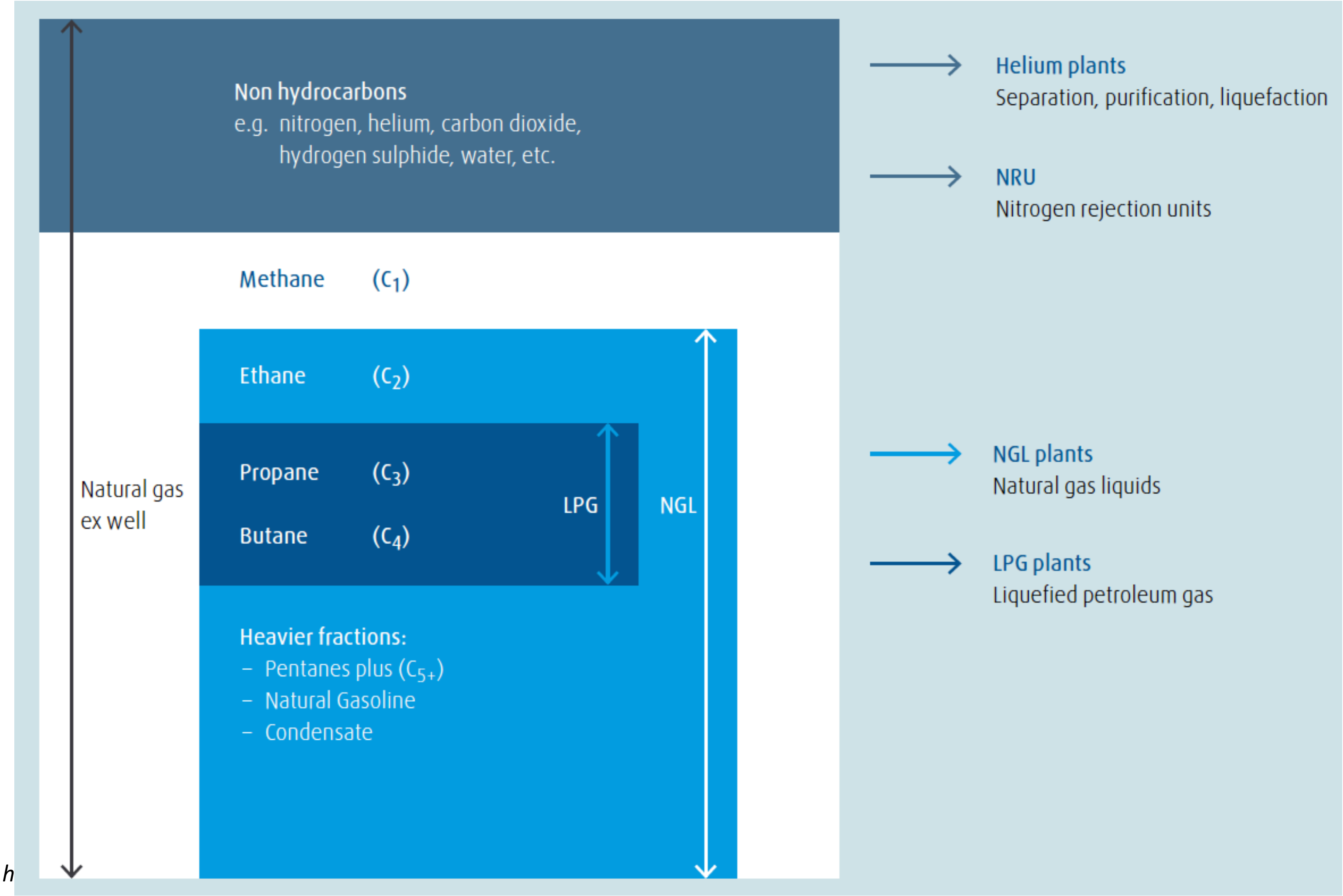
Processamento de Gás Natural



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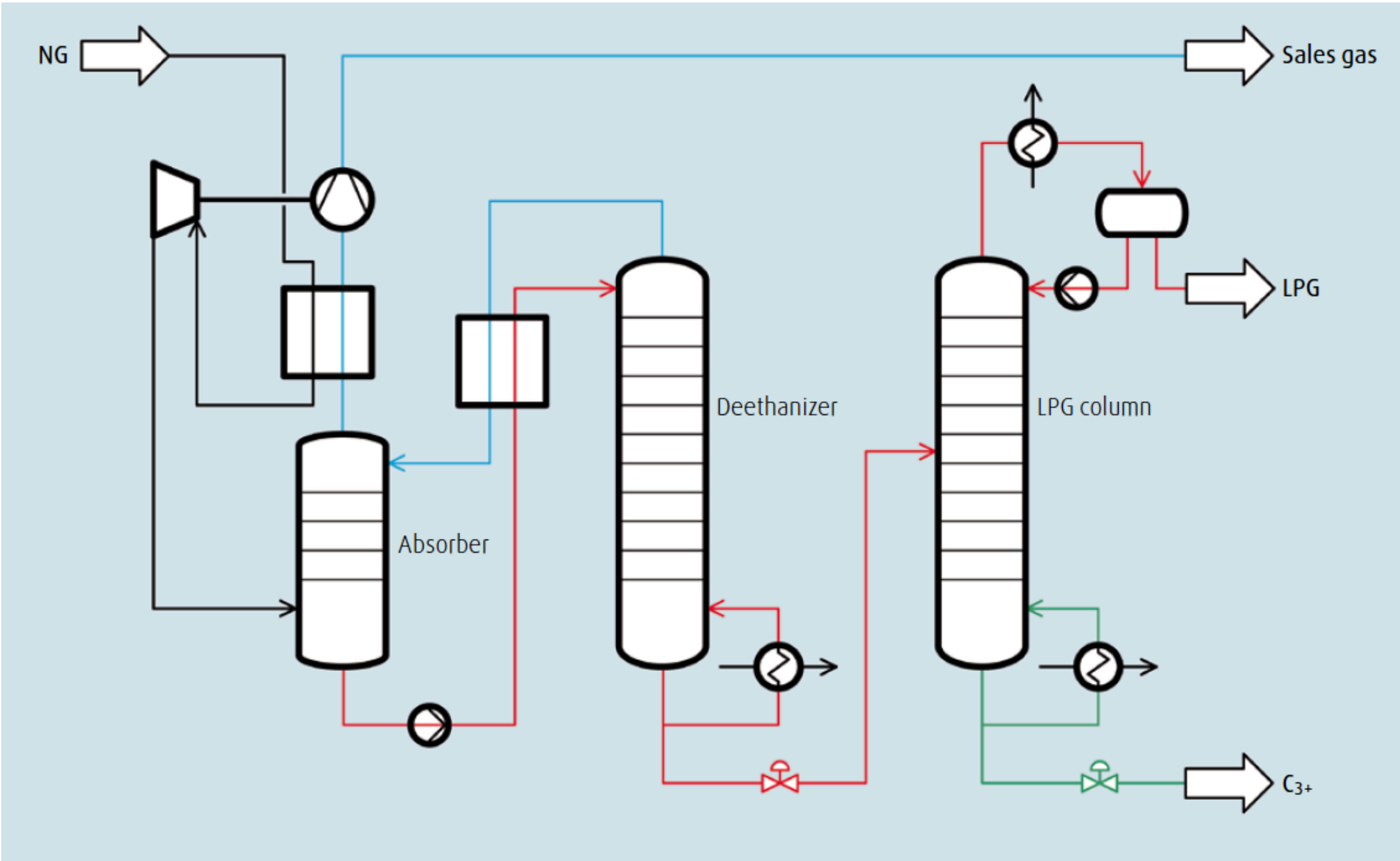
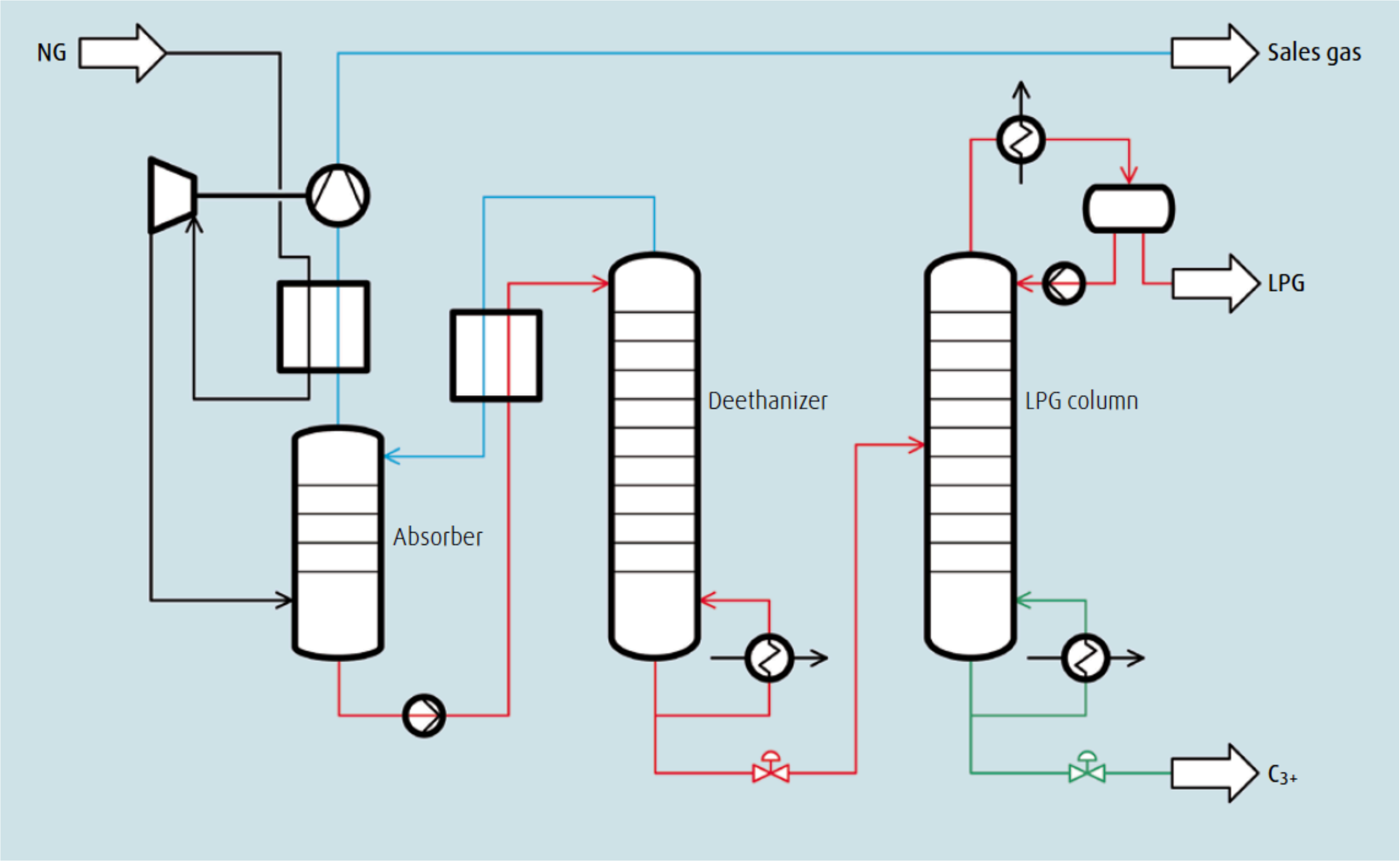
Processamento de Gás Natural



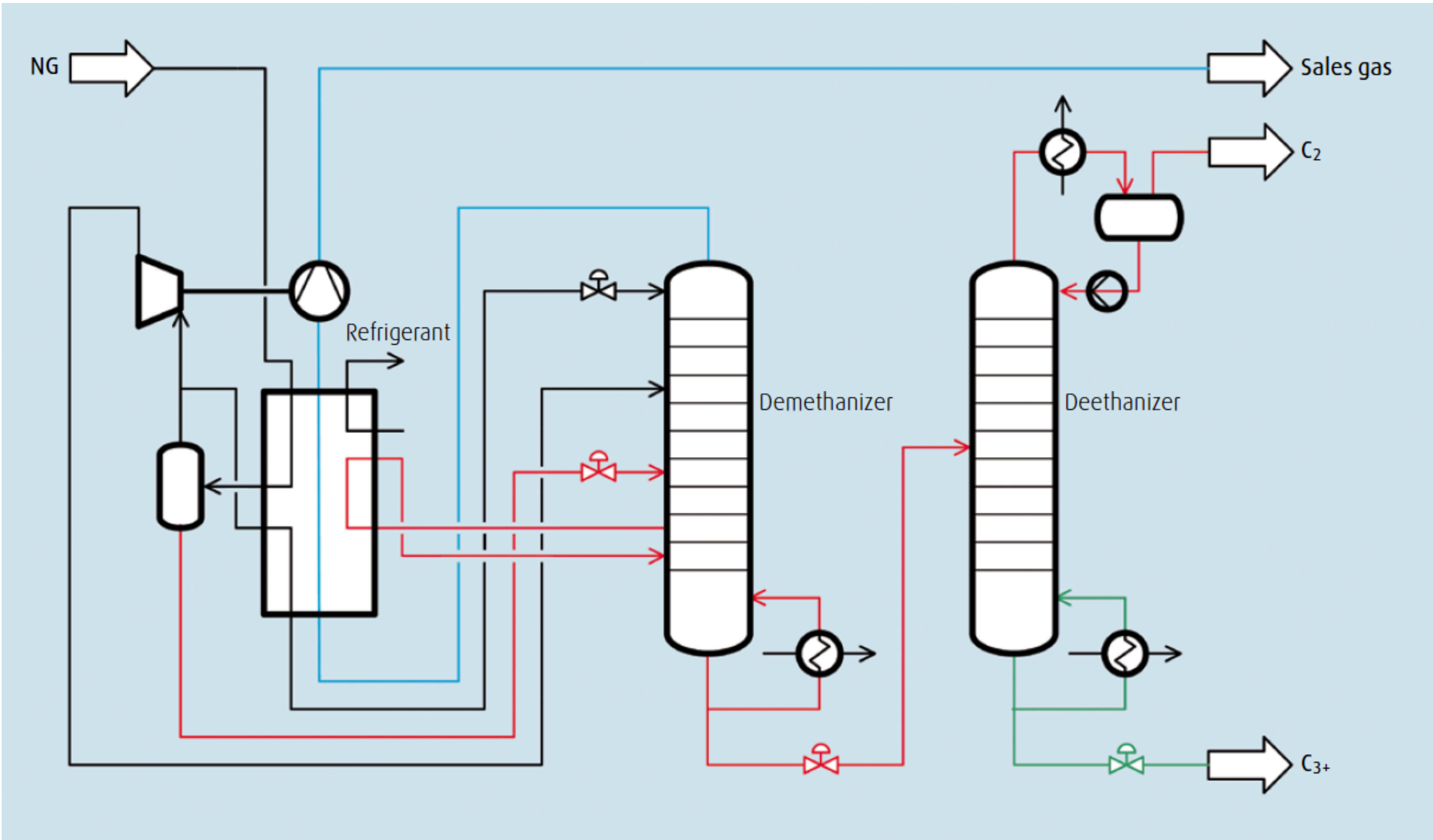
https://www.linde-engineering.com/internet.global.lindeengineering.global/en/images/HE_1_1_e_12_150dpi_NB19_4271.pdf?v=9.0

Processamento de Gás Natural



https://www.linde-engineering.com/internet.global.lindeengineering.global/en/images/HE_1_1_e_12_150dpi_NB19_4271.pdf?v=9.0

Processamento de Gás Natural



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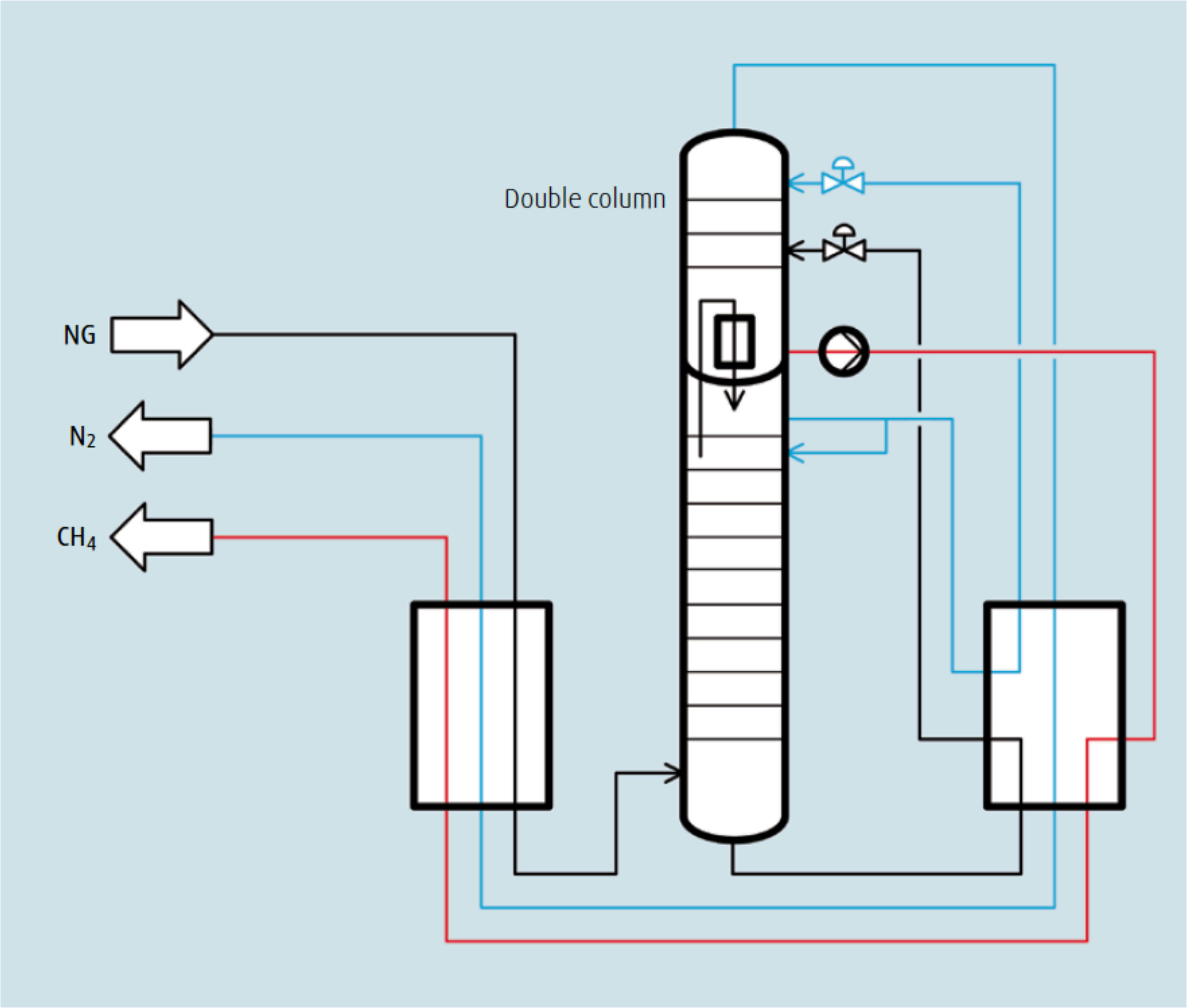
Processamento de Gás Natural



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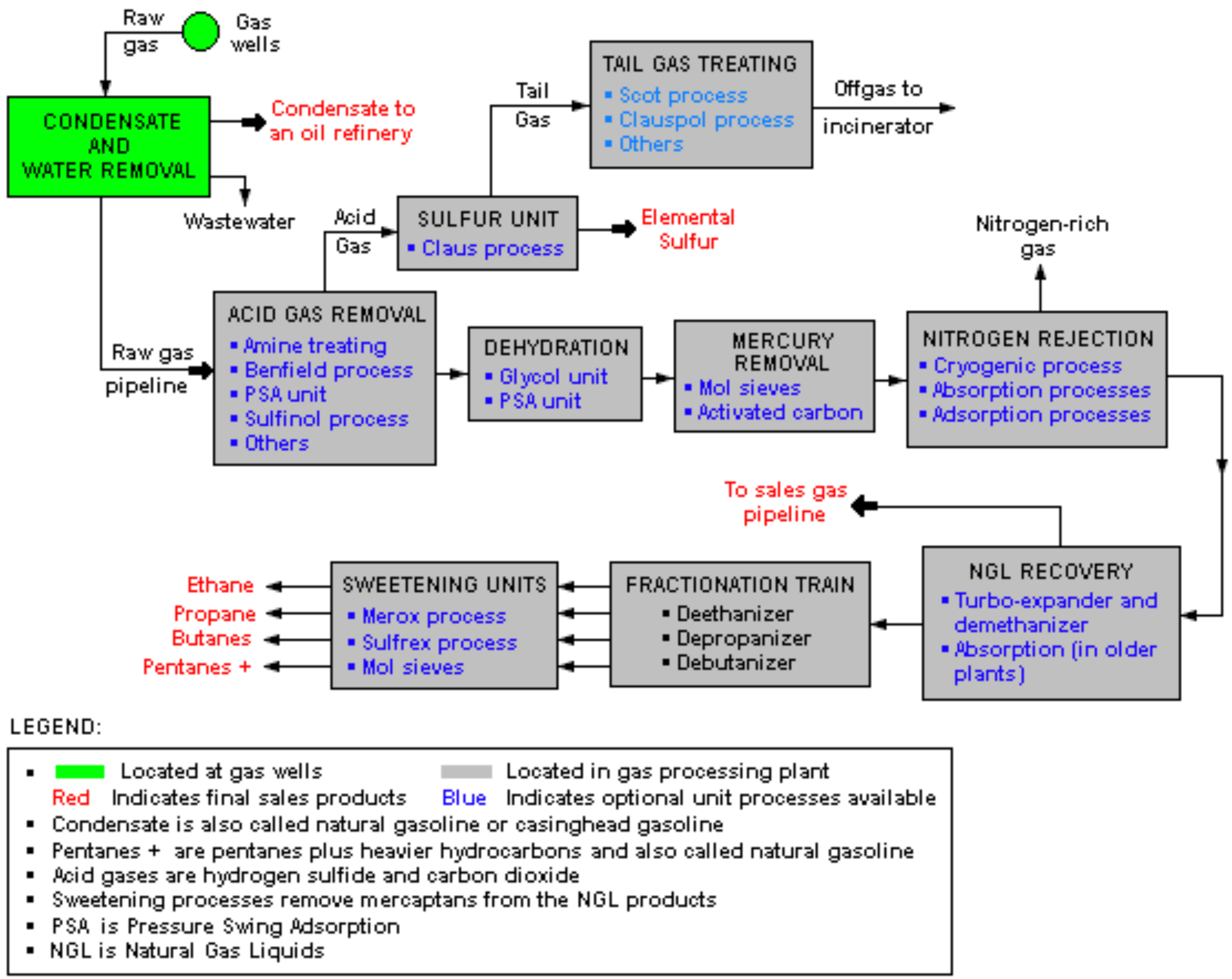
Processamento de Gás Natural

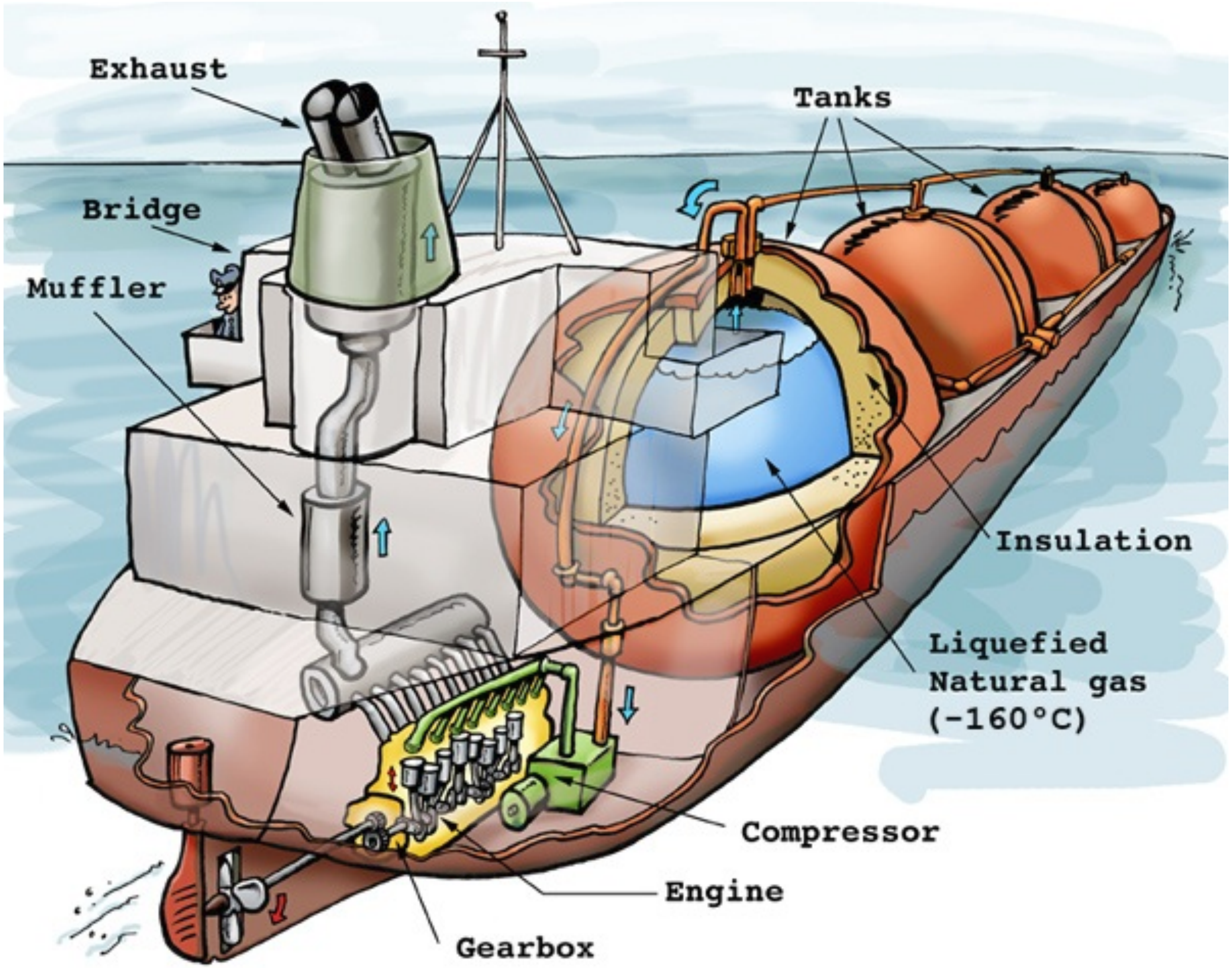


https://en.wikipedia.org/wiki/Natural-gas_processing#/media/File:NatGasProcessing.png

Gás Natural Liquefeito

https://en.wikipedia.org/wiki/LNG_carrier#/media/File:Methanier_aspher_LNGRIVERS.jpg

Gás Natural Liquefeito



https://en.wikipedia.org/wiki/LNG_carrier#/media/File:LNGtanker.jpg

Gás Natural

”Vantagens”:

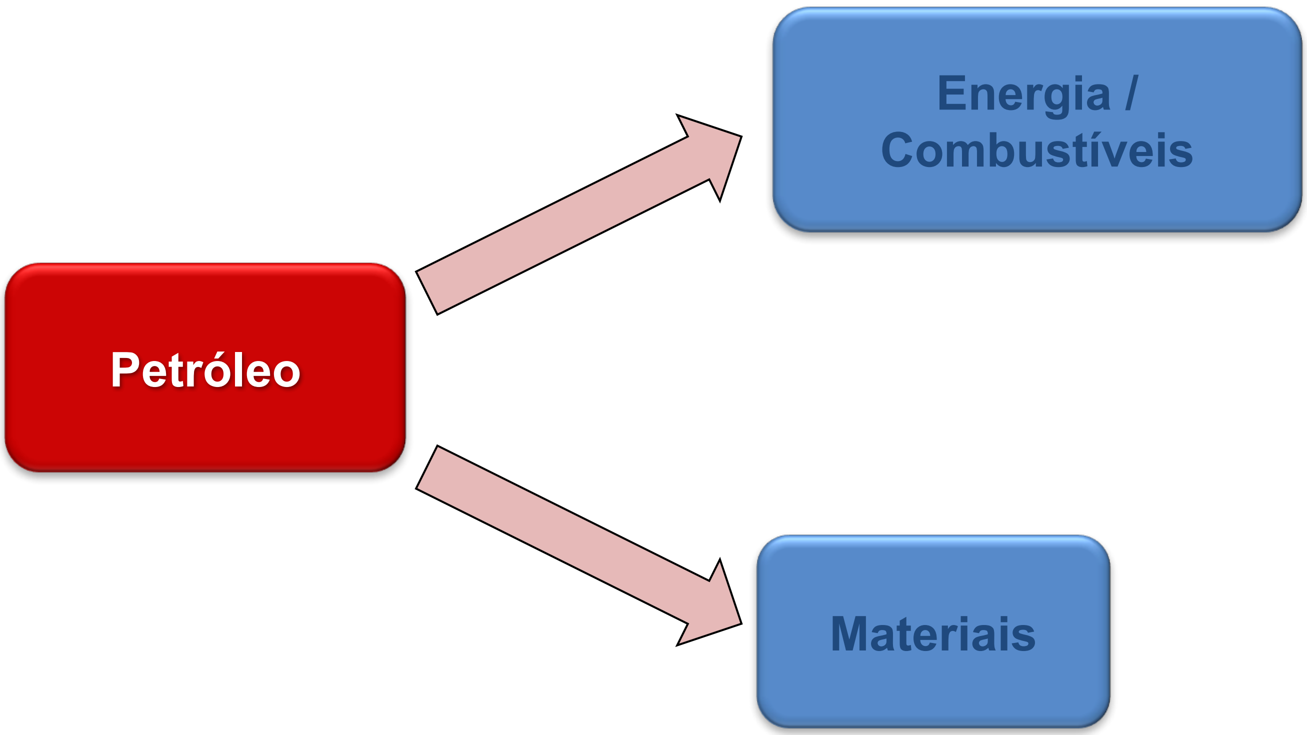
- É o mais ”limpo” dos combustíveis fósseis (menos CO2/unidade de energia);
- Pouco processamento;
- Bombeamento por dutos;
- Menor contribuição para o ”smog fotoquímico”.

”Desvantagens”:

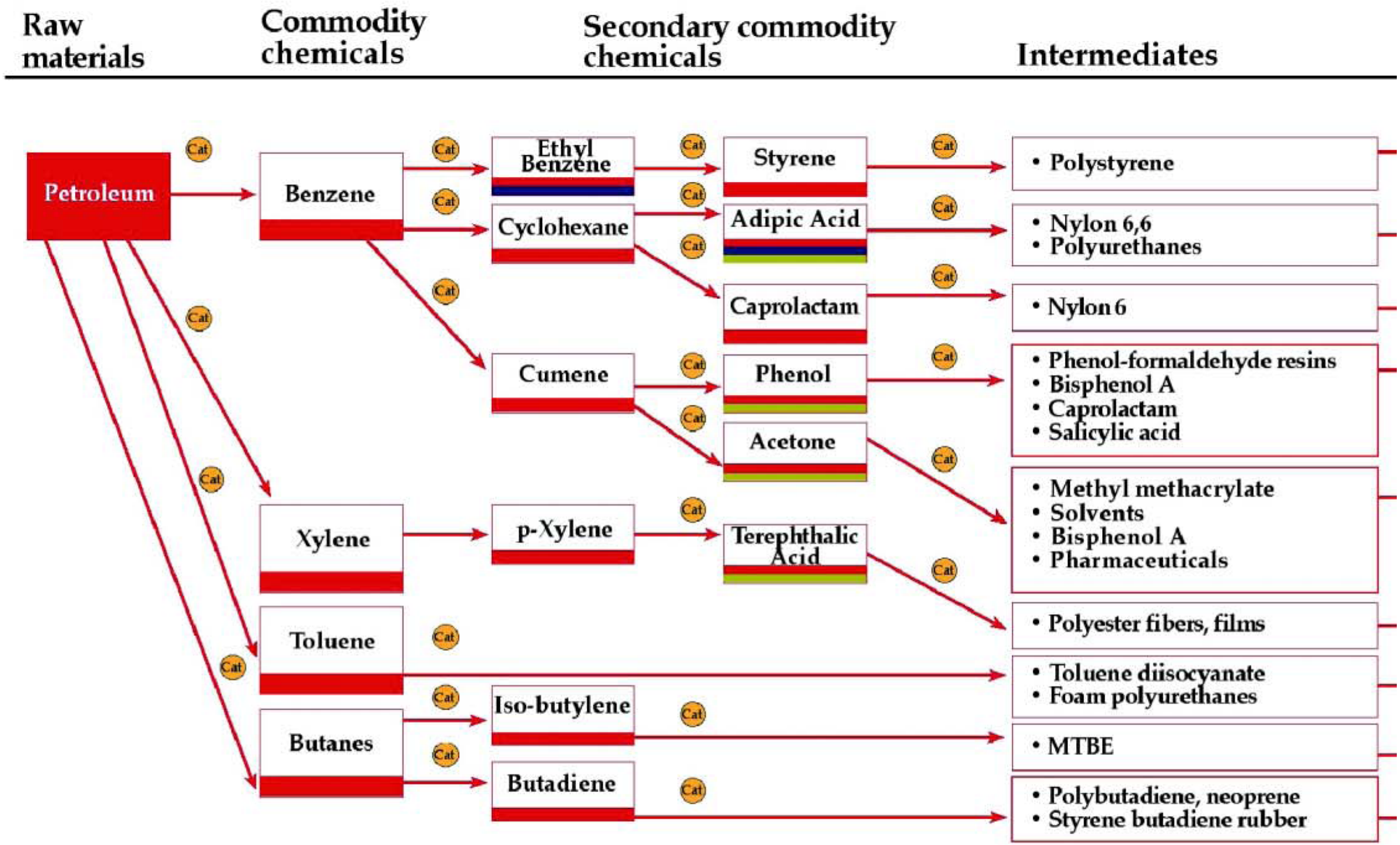
- Mais difícil de transportar (altas pressões e/ou baixas temperaturas);
- Metano é um gás de efeito estufa muito efetivo (20x aprox.) e de meia vida atmosférica relativamente longa;
- Emissões.

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Economia Baseada em Petróleo e Gás Natural



"Plataformas" do Petróleo



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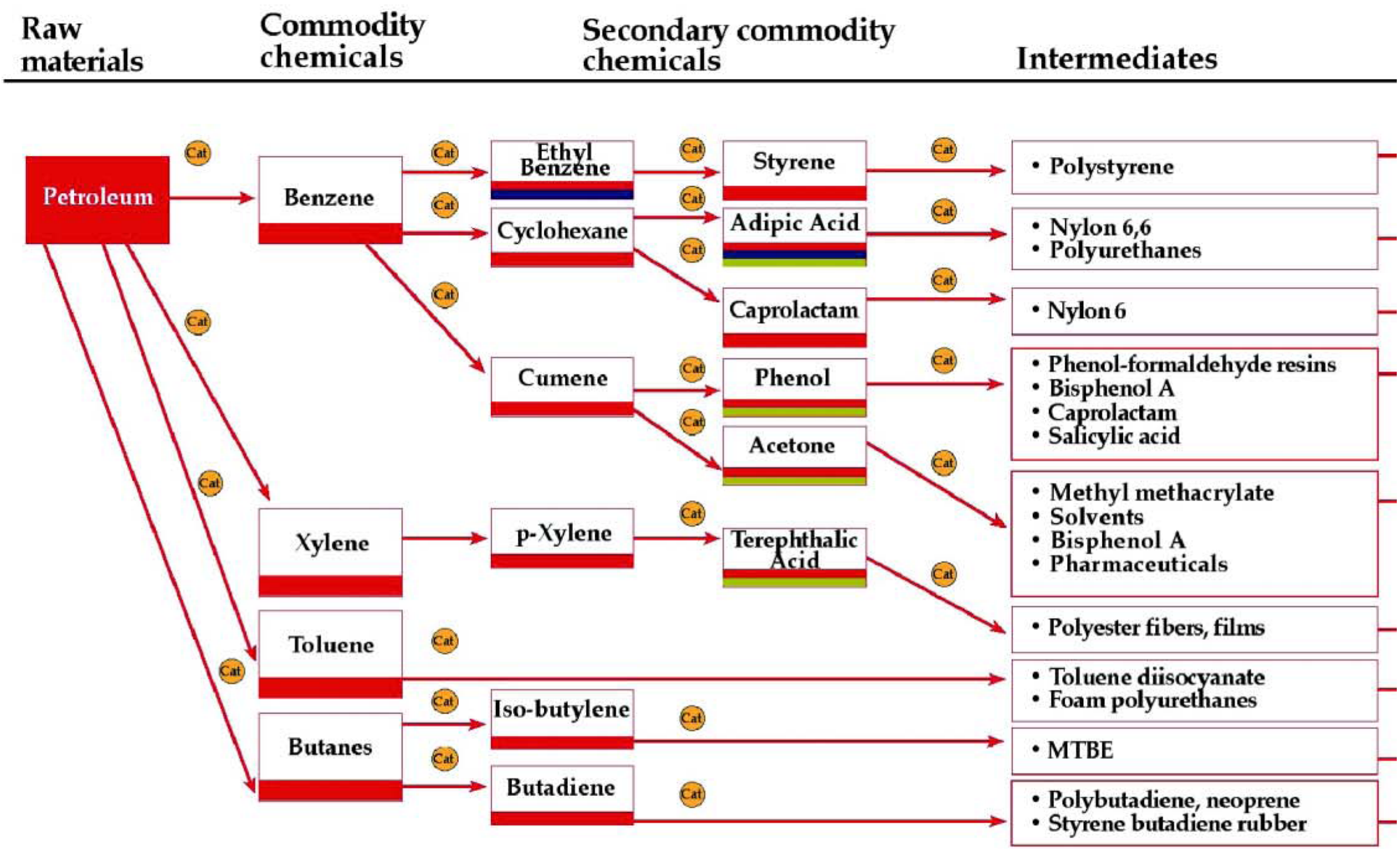
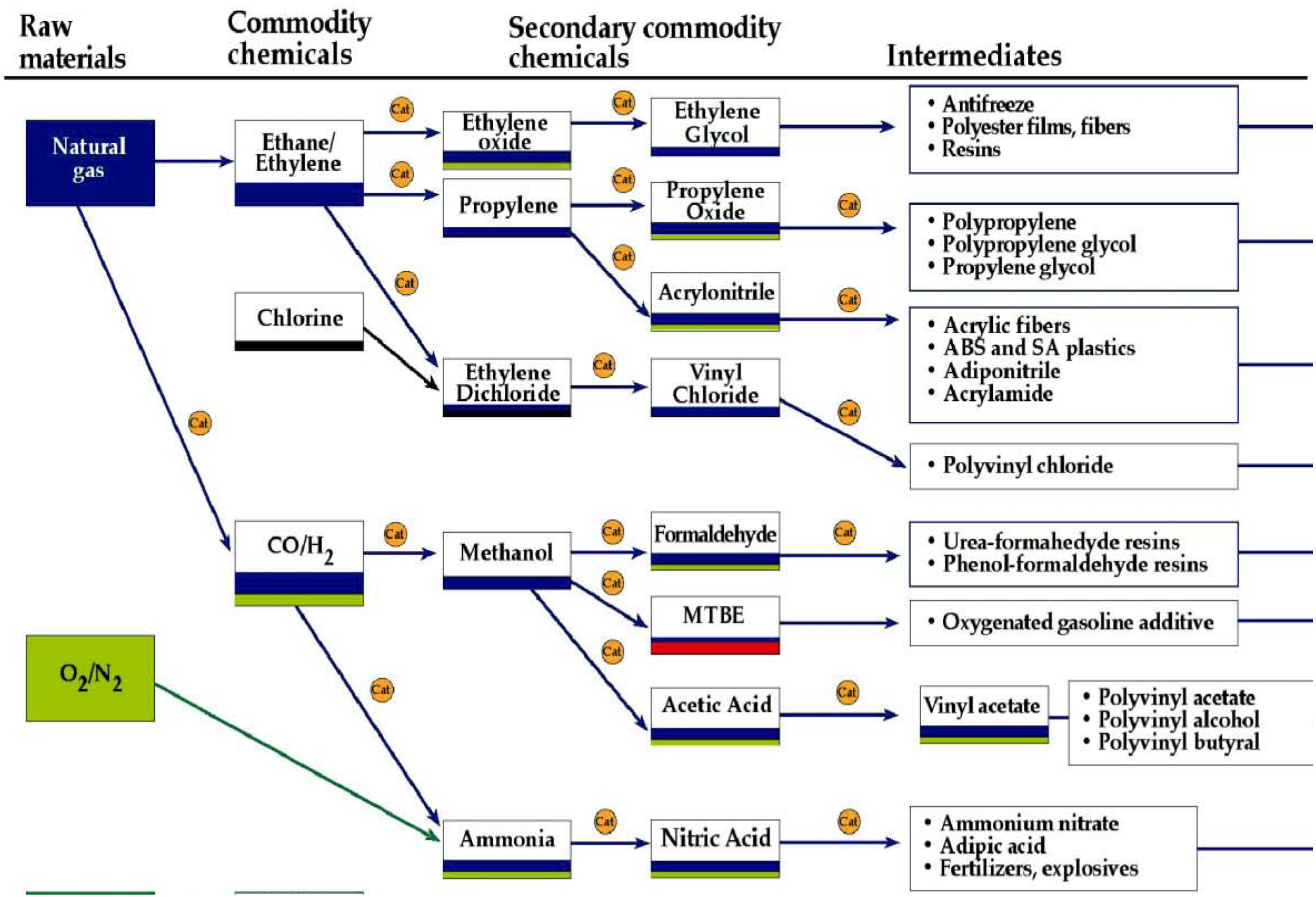
”Plataformas” do Petróleo



Top Value Added Chemicals from Biomass (DOE/GO-102004-1992), U.S. Department of Energy

"Plataformas" do Gás Natural



Top Value Added Chemicals from Biomass (DOE/GO-102004-1992), U.S. Department of Energy

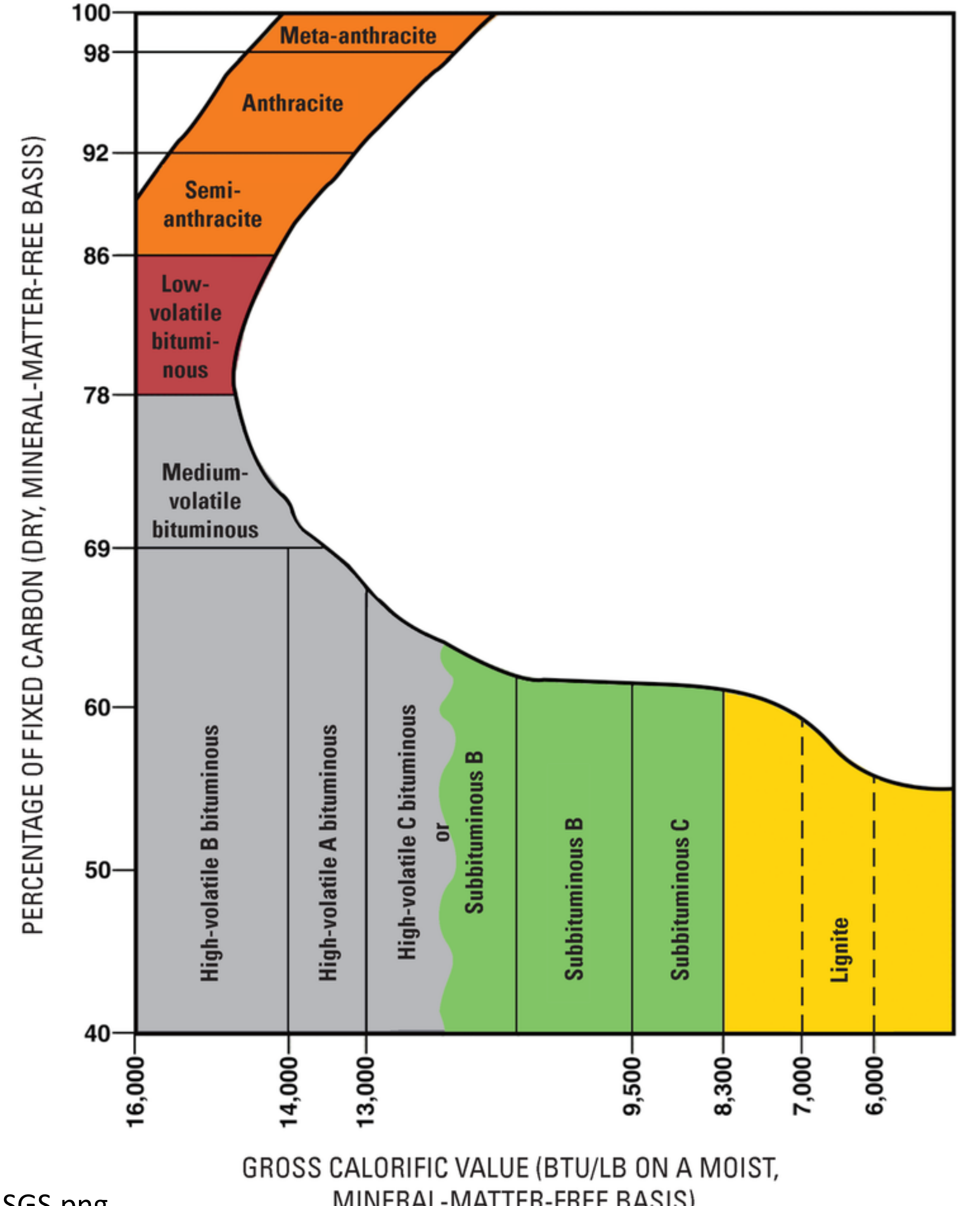
Carvão

https://en.wikipedia.org/wiki/Mining#/media/File:Strip_coal_mining.jpg

Tipos de carvão

http://teachcoal.org/energy-and-you/wp-content/uploads/2012/11/AllCoalSamples-iso.png

Tipos de carvão



https://en.wikipedia.org/wiki/Coal#/media/File:Coal_Rank_USGS.png

Tipos de Carvão

TABLE 2.3 COMPOSITION AND HEAT CONTENT OF COMMON COALS FOUND IN THE UNITED STATES

		Chemical analysis				
Rank	Location by state	Moisture	Volatile matter	Fixed carbon	Ash	Heating value (kJ/g)
Anthracite	Pennsylvania	4.4%	4.8%	81.8%	9.0%	30.5
Bituminous						
Low volatile	Maryland	2.3	19.6	65.8	12.3	30.7
High volatile	Kentucky	3.2	36.8	56.4	3.6	32.7
Sub-bituminous	Wyoming	22.2	32.2	40.3	4.3	22.3
Lignite	North Dakota	36.8	27.8	30.2	5.2	16.2

Source: U.S. Bureau of Mines (1954). *Information Circular No. 769* (Washington, DC: U.S. Department of Interior).

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Carvão

"Vantagens":

- Depósitos muito grandes;
- Barato para minerar e transportar;
- Uso para gerar outros combustíveis.

"Desvantagens":

- Transporte menos conveniente (sólido);
- Problemas ambientais e de saúde na mineração;
- Emissões (NOx, SO2, CO2 – maior emissão por unidade de energia – razão C/H).

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Emissões do Carvão

Average Sulfur Content of Coal by Rank		
Rank	% of total coal reserves	% with sulfur content > 1%
Anthracite	0.9	2.9
Bituminous	46.0	70.2
Sub-bituminous	24.7	0.4
Lignite	28.4	9.3
Total, all ranks	100.0	35.0

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Emissões do Carvão

Average Sulfur Content of Coal by Rank		
Rank	% of total coal reserves	% with sulfur content > 1%
Anthracite	0.9	2.9
Bituminous	46.0	70.2
Sub-bituminous	24.7	0.4
Lignite	28.4	9.3
Total, all ranks	100.0	35.0

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Captura de CO_2

http://www.co2industries.com/data/attachment/201611/29/fb8038cd13d1ef083dd90b568f29ed62.jpg

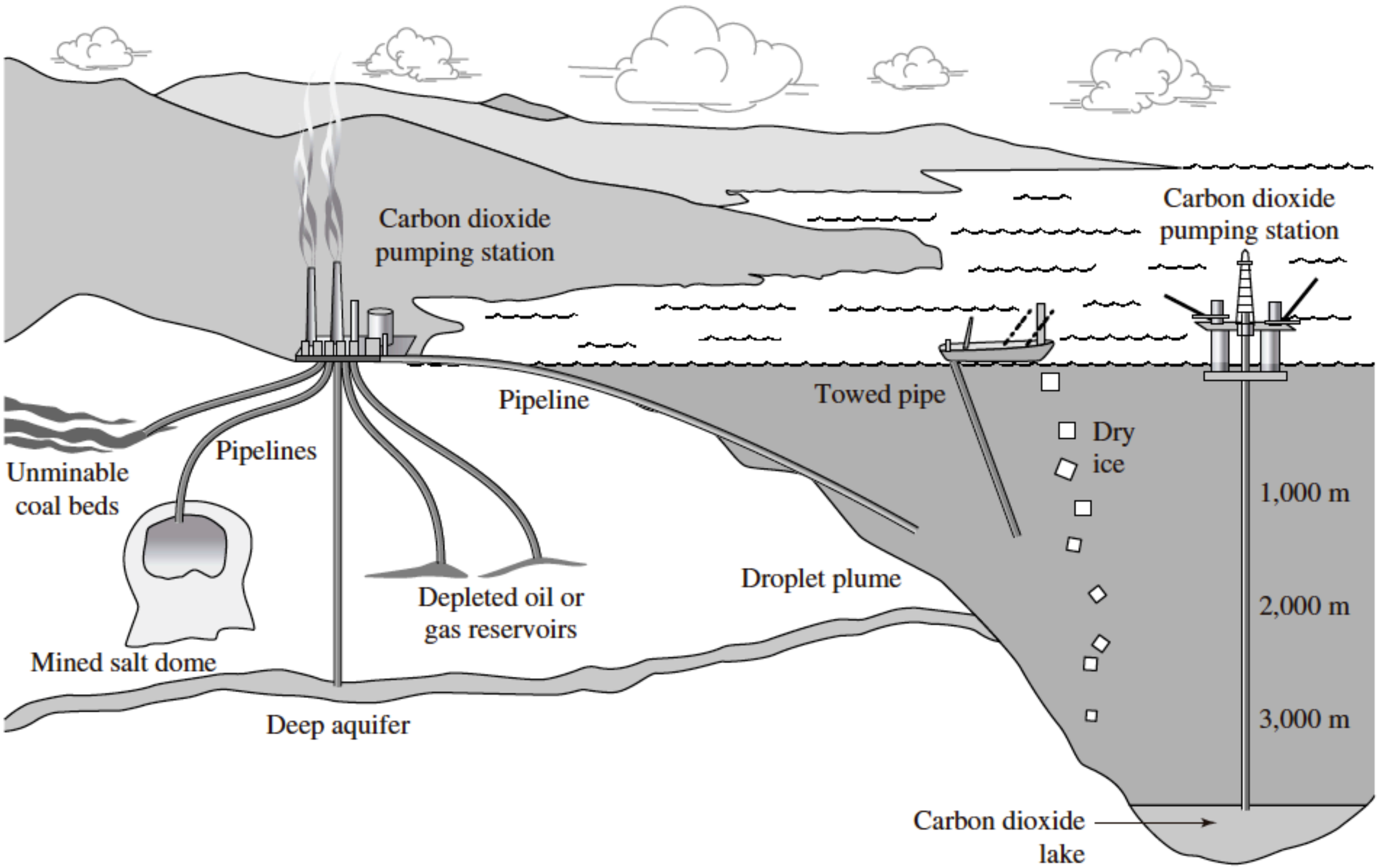
Captura de CO2

Absorção por aminas (e desorção térmica)

$$R_3N + CO_2 = R_3NCO_2$$

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.

Captura de CO2



Storage underground	Advantages	Disadvantages	Storage in oceans	Advantages	Disadvantages
Coal beds	Potentially low costs	Immature technology	Droplet plume	Minimal environmental effects	Some leakage
Mined salt domes	Custom designs	High costs	Towed pipe	Minimal environmental effects	Some leakage
Deep saline aquifers	Large capacity	Unknown storage integrity	Dry ice	Simple technology	High costs
Depleted oil or gas reservoirs	Proven storage integrity	Limited capacity	Carbon dioxide lake	Carbon will remain in ocean for thousands of years	Immature technology

Spiro & Stigliani, Chemistry of the Environment, 2nd ed., 2002.