VI ENCONTRO DA ESCOLA
BRASILEIRA DE
QUÍMICA VERDE

Biorrefinarias: A matéria-prima
definindo o processo

26 e 27 - Set/2016
CTBE/CNPEM, Campinas-SP

BIORREFINARIA DE MICROALGAS

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UNIVERSIDADE FEDERAL DO
RIO DE JANEIRO - BRASIL

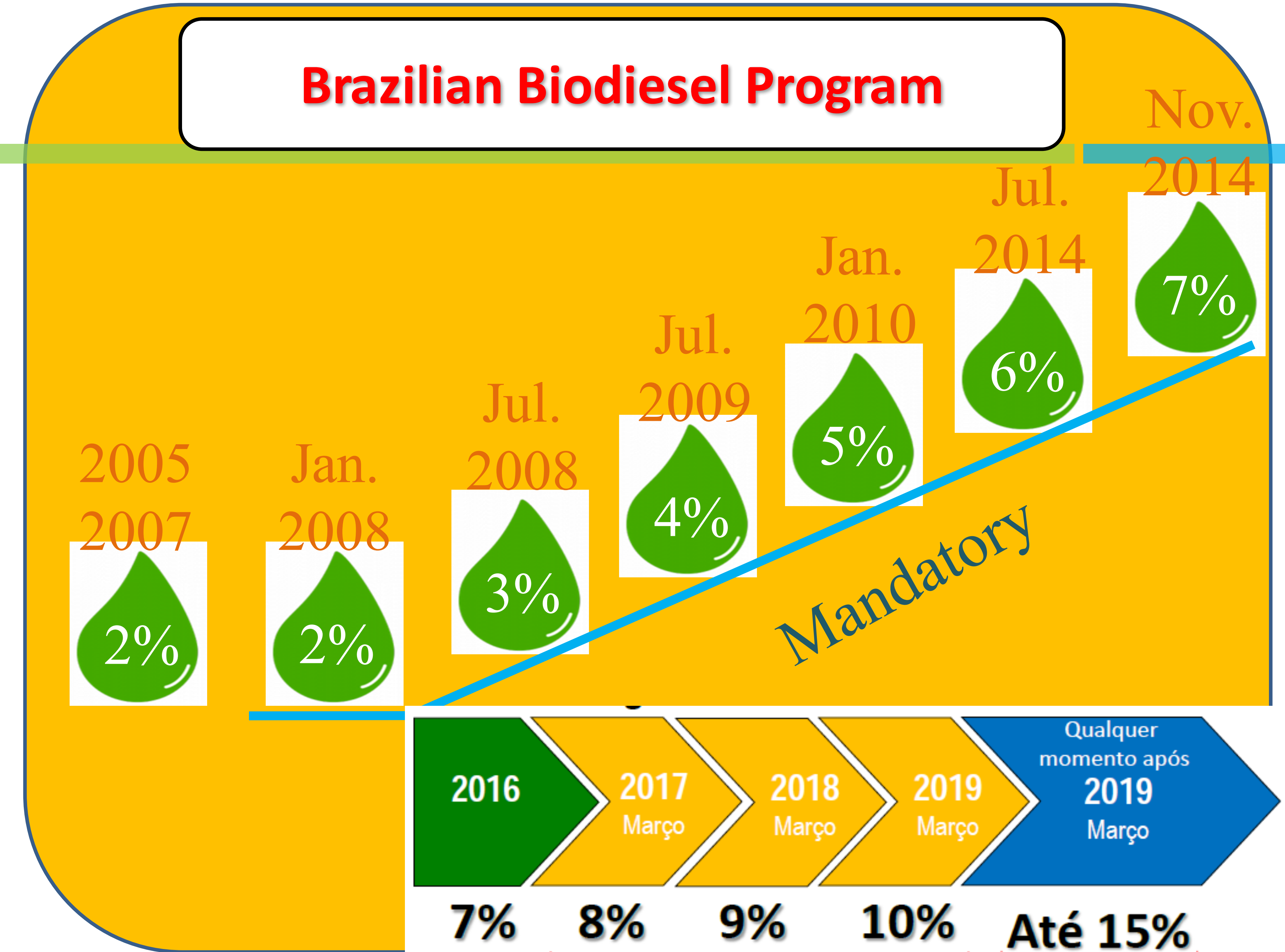
Campinas, Setembro 2016

TOP FIVE COUNTRIES

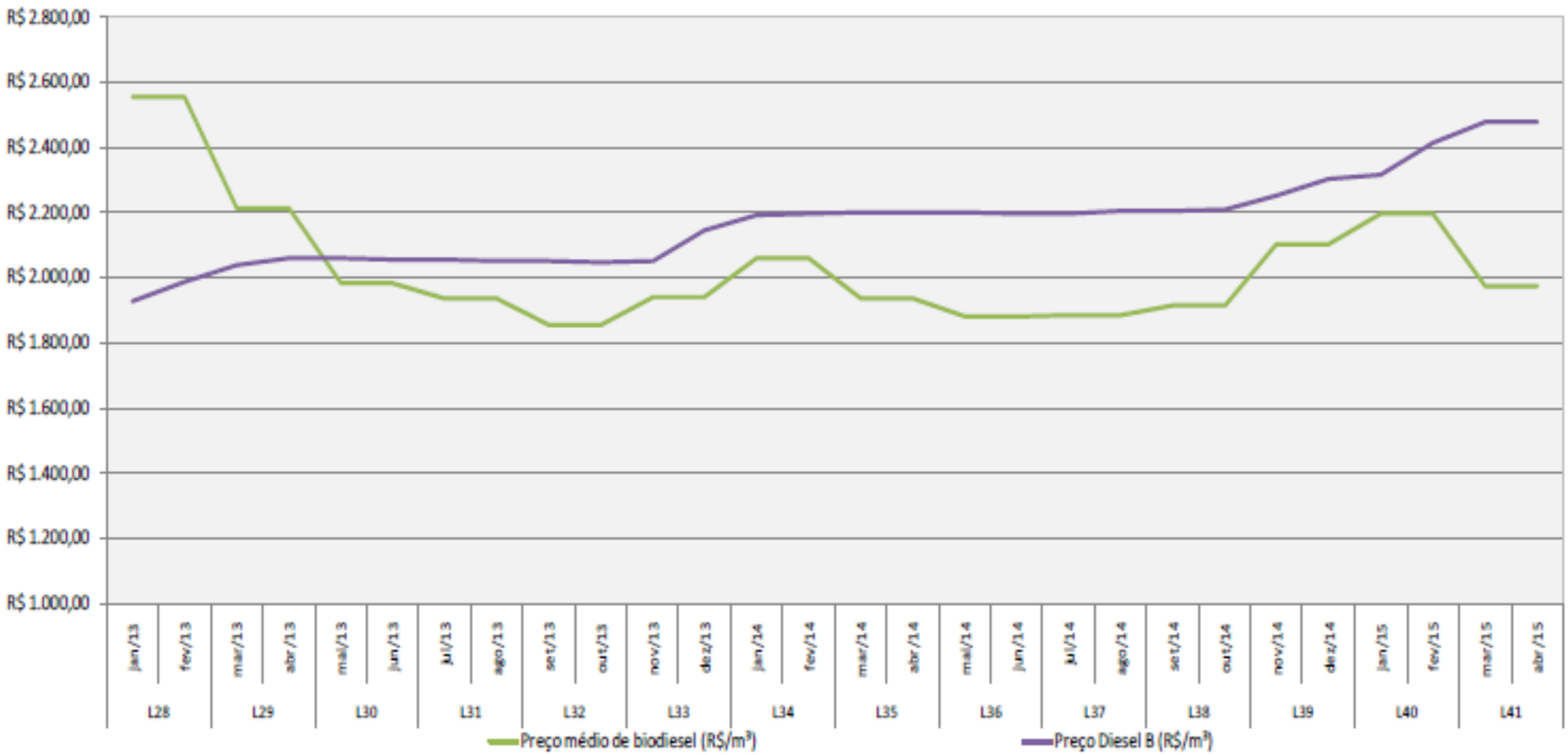
ANNUAL INVESTMENT / NET CAPACITY ADDITIONS / PRODUCTION IN 2014

	1	2	3	4	5
Investment in renewable power and fuels (not including hydro > 50 MW)	**China**	United States	Japan	United Kingdom	Germany
Investment in renewable power and fuels per unit GDP[1]	**Burundi**	Kenya	Honduras	Jordan	Uruguay
Geothermal power capacity	**Kenya**	Turkey	Indonesia	Philippines	Italy
Hydropower capacity	**China**	Brazil	Canada	Turkey	India
Solar PV capacity	**China**	Japan	United States	United Kingdom	Germany
CSP capacity	**United States**	India	–	–	–
Wind power capacity	**China**	Germany	United States	Brazil	India
Solar water heating capacity[2]	**China**	Turkey	Brazil	India	Germany
Biodiesel production	**United States**	Brazil	Germany	Indonesia	Argentina
Fuel ethanol production	**United States**	Brazil	China	Canada	Thailand

SOURCE: REN21 - 2015


Brazilian Biodiesel Program
2005 2007
2%
Jan. 2008
2%
Jul. 2008
3%
Jul. 2009
4%
Jan. 2010
5%
Jul. 2014
6%
Nov. 2014
7%
Mandatory
2016
2017 Março
2018 Março
2019 Março
Qualquer momento após 2019 Março
7%
8%
9%
10%
Até 15%

Comparação entre Preço Médio do Biodiesel e Diesel - Brasil



Fonte: ANP

Dependência externa

15 BI | 28 BI

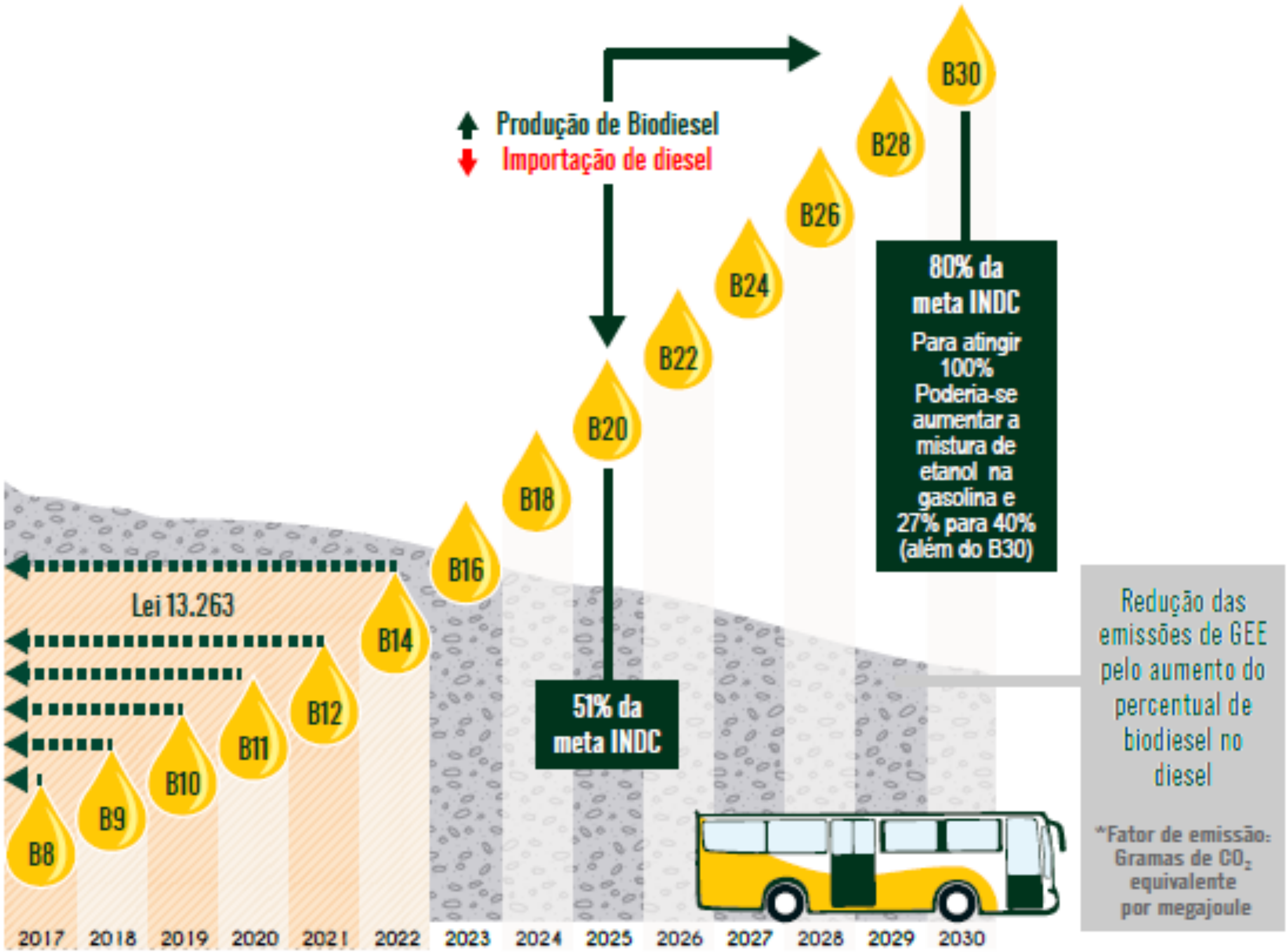
	2015 Real	2026 Estimativa	2030 Estimativa
Óleo diesel A	117	264 / 205	483 / 424
Ciclo Otto	32	198	408
Subtotal	149	462 / 403	891 / 832
QAV	23	100	120
GLP	30	60	70
Nafta	121	120	120
Total geral	323	742 / 683	1.201 / 1.142

Maior déficit global

*Em mil b/d. Os dados em vermelho não consideram a entrada em operação do COMPERJ

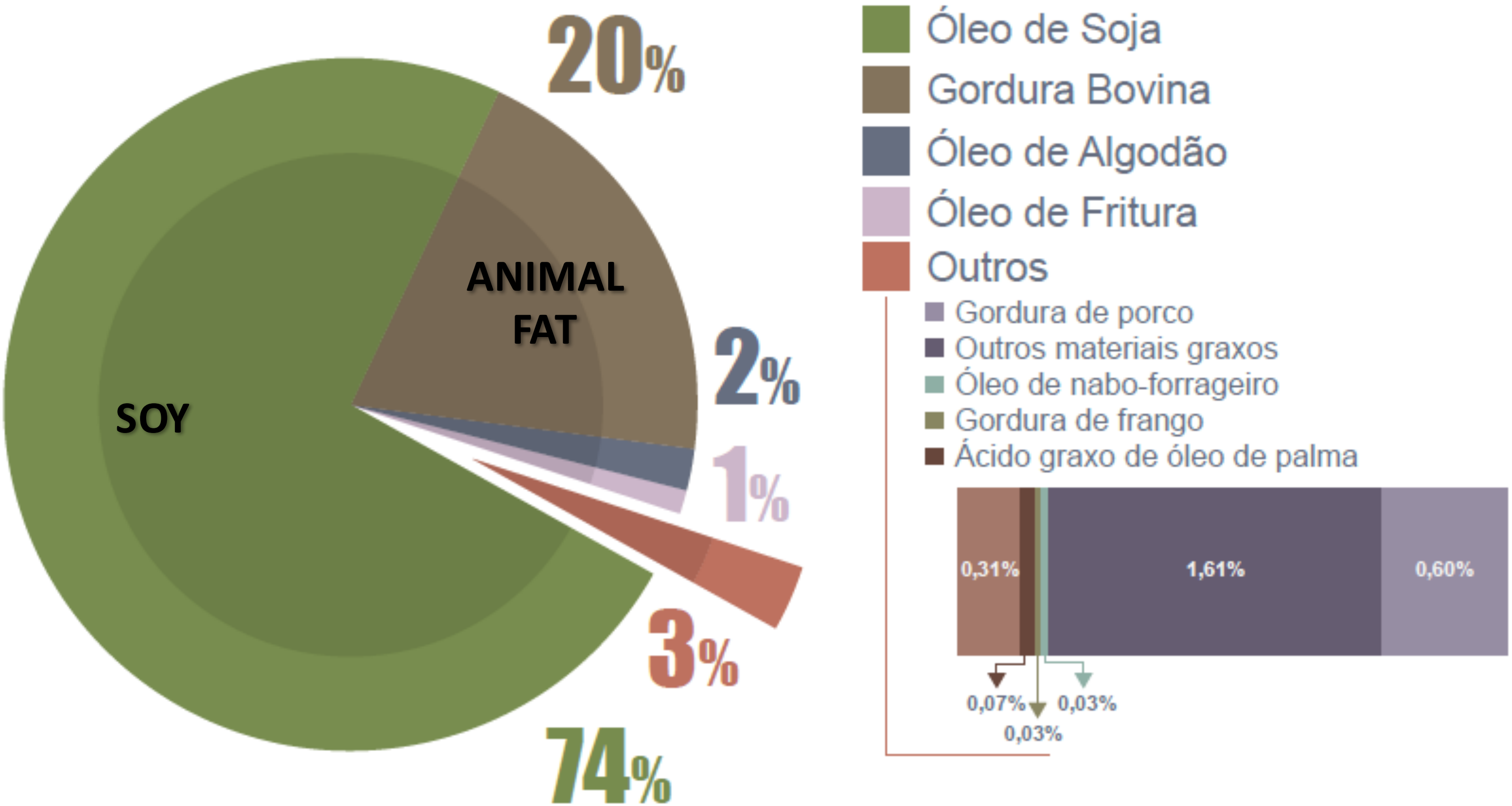
Fonte: 'Cenário Atual do Abastecimento de Combustíveis Automotivos no Brasil, ANP, Abril/2016'

FUTURO DO BIODIESEL



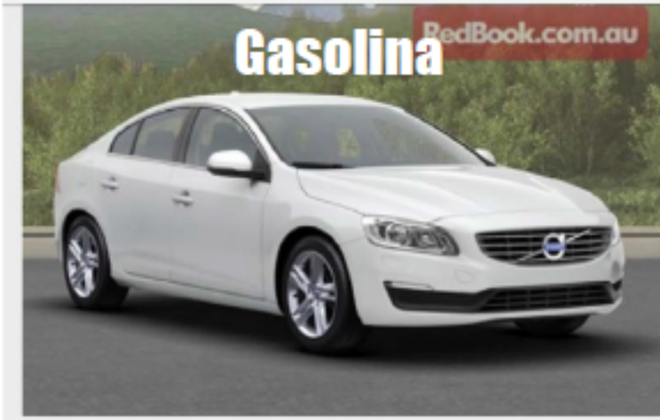
Fonte: Ubrabio

BIODIESEL FEEDSTOCK PROFILE



Fonte: ANP

Dois veículos de mesma potência
Gasolina vs. Diesel



Volvo S60 T4 Kinetic Sedan 4dr Geartronic 6sp 2.0T [MY16]

$56,717 or $206 PER WEEK*

- 2.0 L, 140KW (Petrol - Premium ULP)
- Sports Automatic
- 4 Doors, 5 Seats
- 5.8 L/ 100 km **17 km/L**
- Front Wheel Drive

Volvo S60 D4 Kinetic Sedan 4dr Adap Geartronic 8sp 2.0DTT [MY16]

$58,487 or $212 PER WEEK*

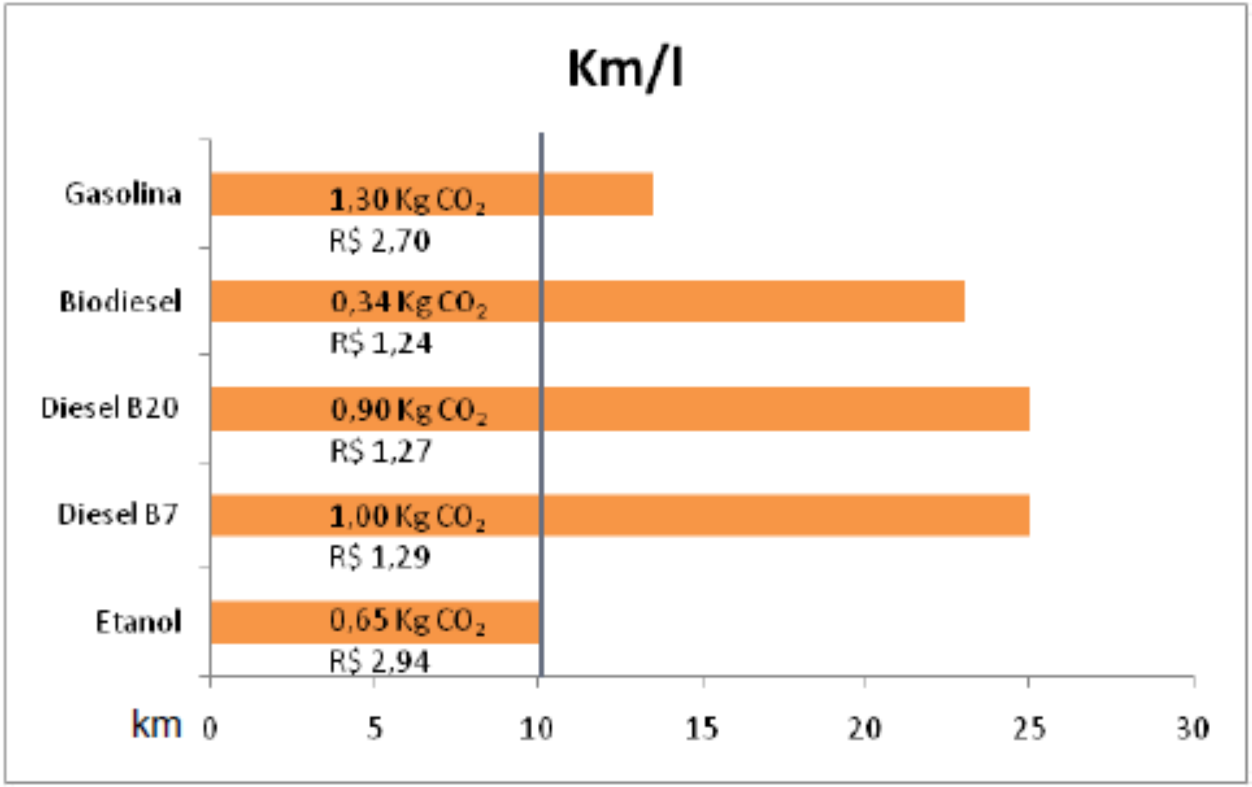
- 2.0 L, 140KW (Diesel)
- Sports Automatic
- 4 Doors, 5 Seats
- 4.2 L/ 100 km **24 km/L**
- Front Wheel Drive

Veículo Diesel 40% mais econômico!

Comparado com a Gasolina Brasileira (E27), a diferença é ainda maior

Fonte: RedBook.com.au

Economicidade dos Combustíveis
Emissões de CO_2/10 Km e Gasto em Reais/10 Km



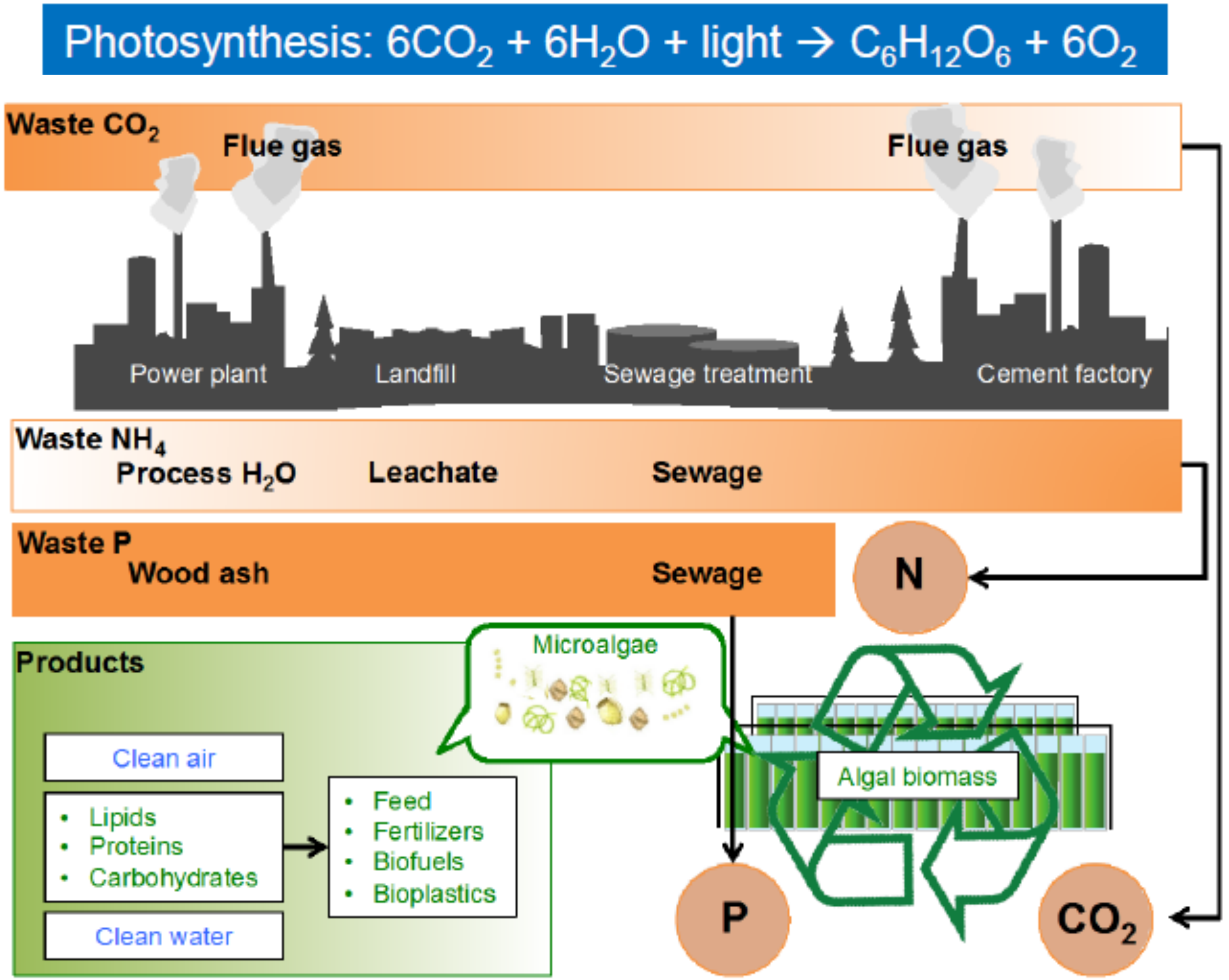
*Veículo Sedan 1.5

Ubrabio
União Brasileira do Biodiesel e Bioquerosene

Quanto representa cada ônibus utilizando B20?

Um ônibus urbano gasta em média 44 mil litros de diesel por ano

- Se usar B20, isso representa uma redução de:
  - 18 ton de CO_2/ônibus por ano!
  - Equivale a plantar 132 novas árvores por ano !! Para cada ônibus!!



Photosynthesis: $6CO_2 + 6H_2O$ + light → $C_6H_{12}O_6 + 6O_2$
Waste CO_2
Flue gas
Flue gas
Power plant
Landfill
Sewage treatment
Cement factory
Waste NH_4
Process H_2O
Leachate
Sewage
Waste P
Wood ash
Sewage
N
Products
Microalgae
Clean air
Lipids
Proteins
Carbohydrates
Feed
Fertilizers
Biofuels
Bioplastics
Clean water
Algal biomass
P
CO_2

MICROALGAS


Lake Kossorom
(Chad, Africa)
…also collected since
centuries from natural blooms
(Abdulqader, Barsanti, Tredici, 2000)

“Raceways”

Problems: Evaporation + Contamination

Microalgae produced in Photobioreactors (UFRJ)

Lipids and Proteins: high production rates

Biomass: 200% growing/day

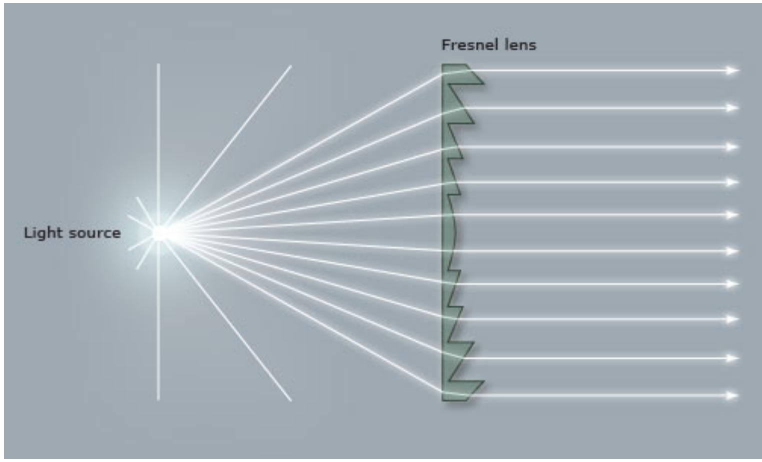
Buggypower – Ilha da Madeira

Photobioreactors with Sunlight Concentrators

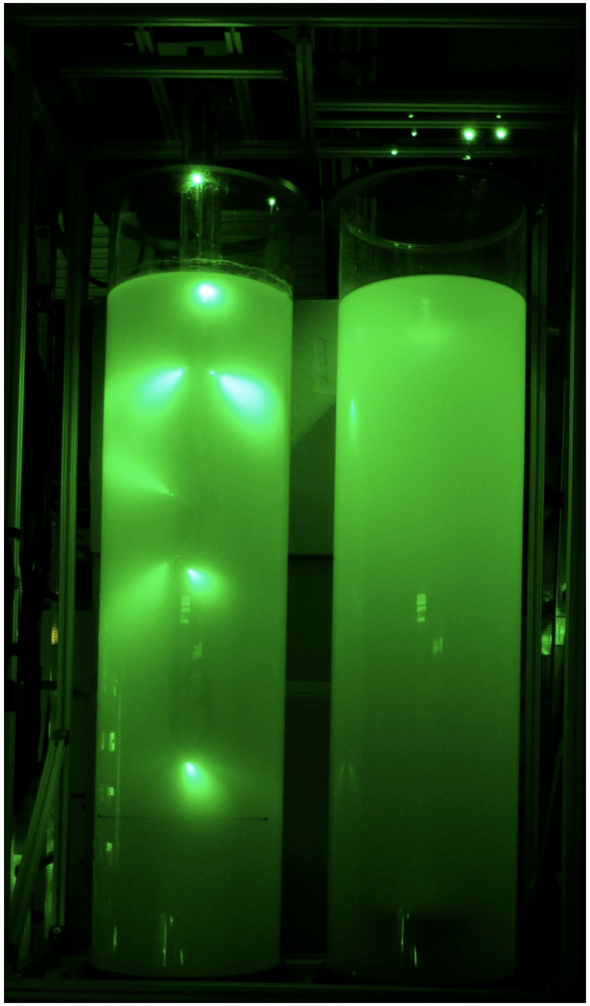
PBR with sunlight concentrator

Sunlight Prisms

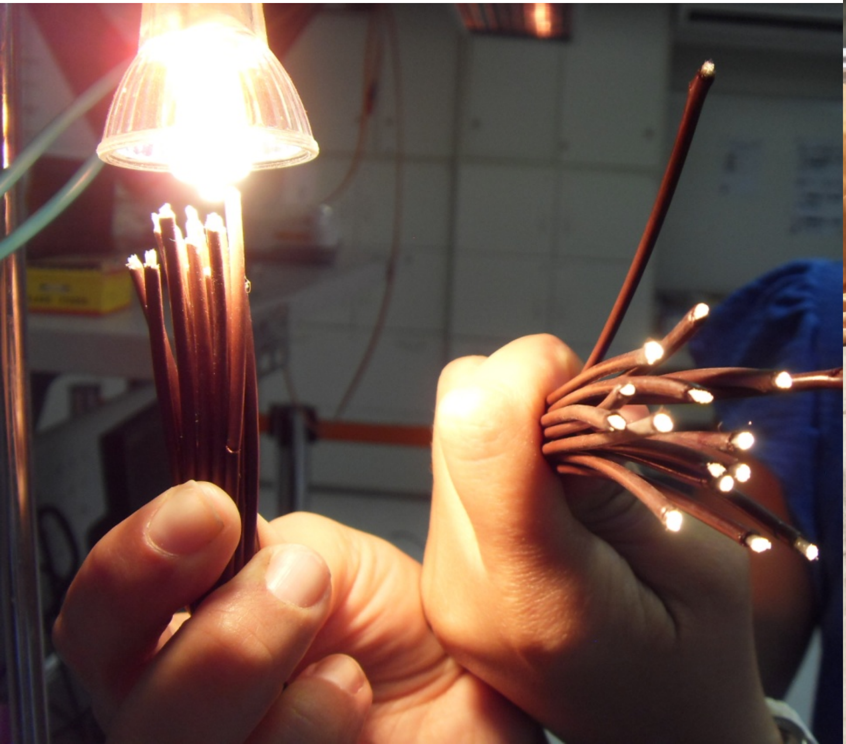
Fresnel Lens



Optical Fibers



30 Liters System



Concentrated Biomass

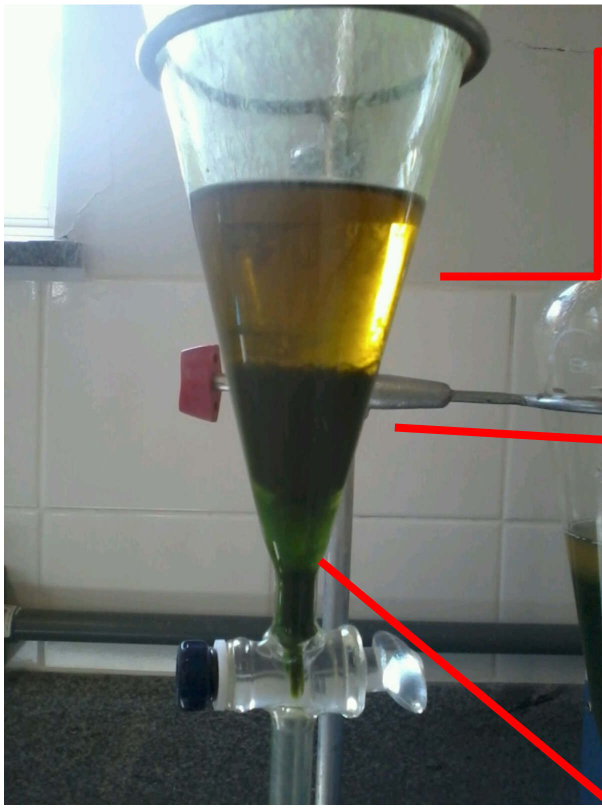
Wet Biomass
Monoraphidium sp. (MORF-1)

Wet Biomass
Chlamydomonas sp.

Lipid Extraction

Milk Homogenizer
Pressure Pulses: 100 bar
Room Temperature.

Algal lipids

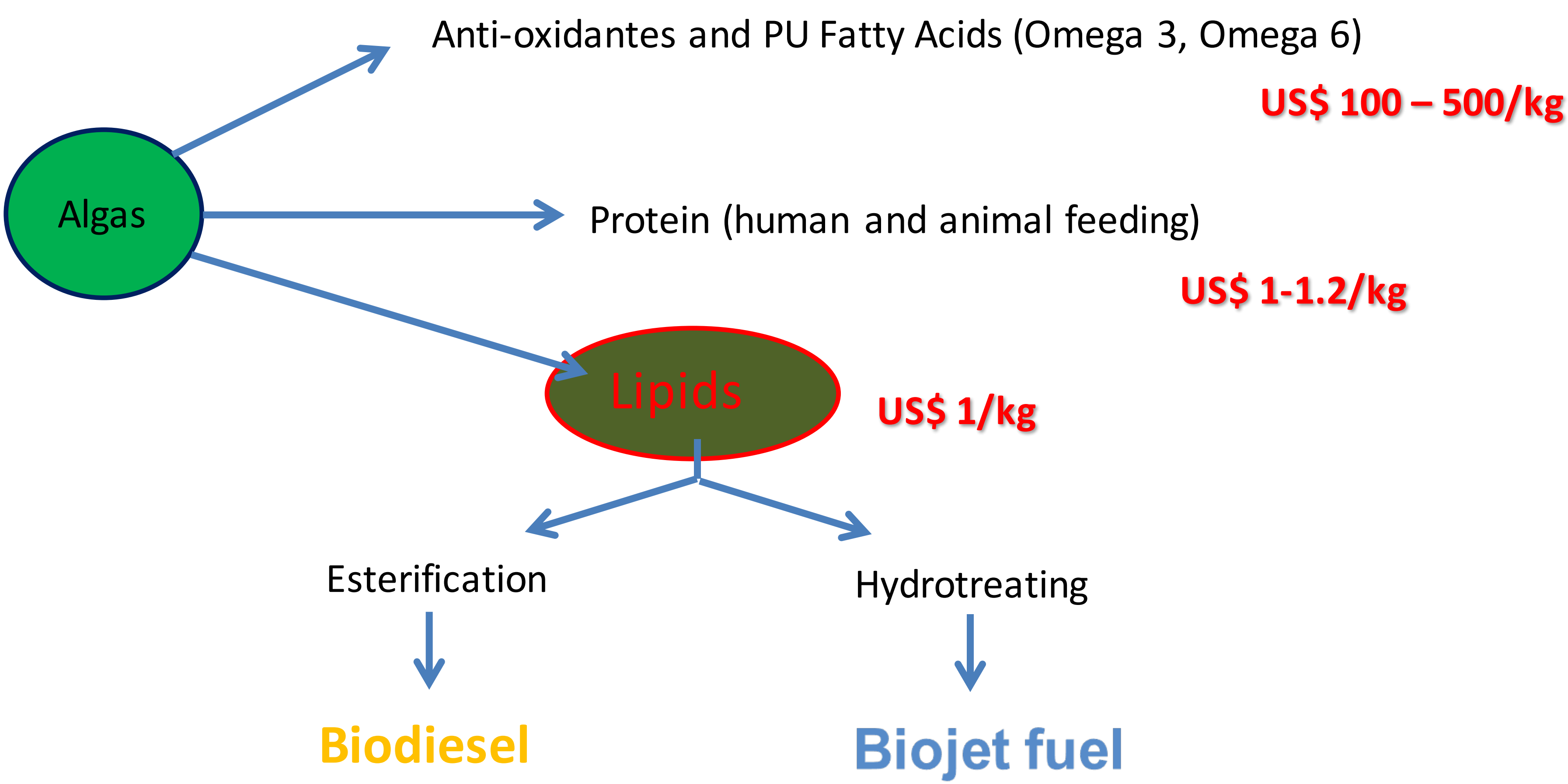


Lipid Phase

Wet Protein Meal

Aquous Phase

Biorefinery Treatment for Algae Biomass



Antioxidantes (US$ +500/kg)   Ômega 3 (US$ 100/kg)

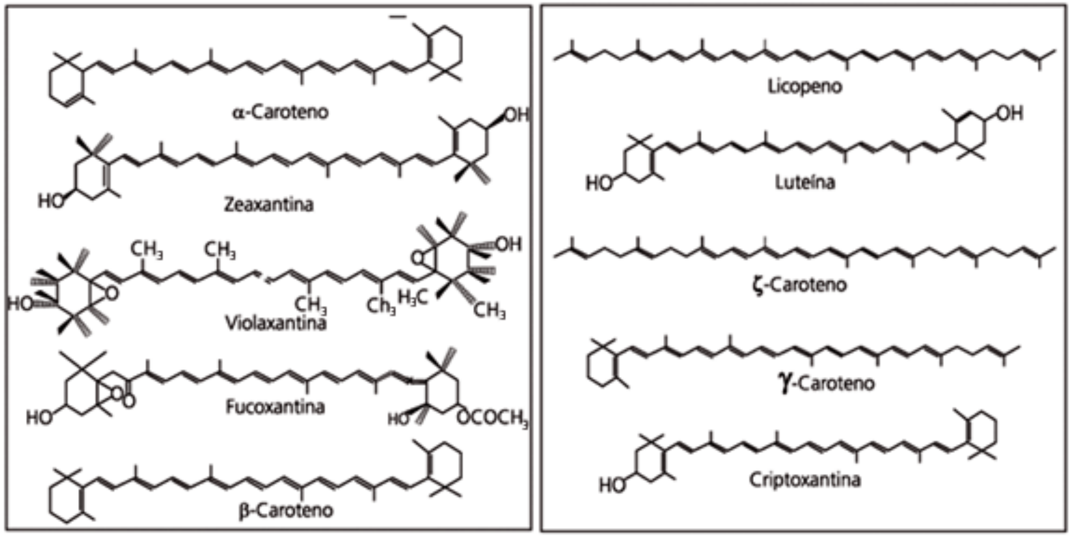
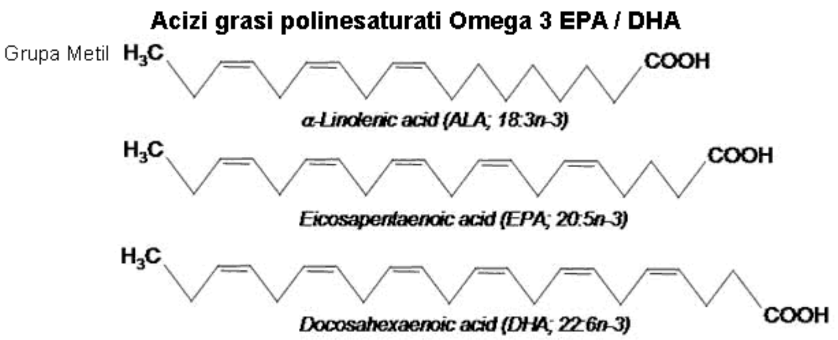
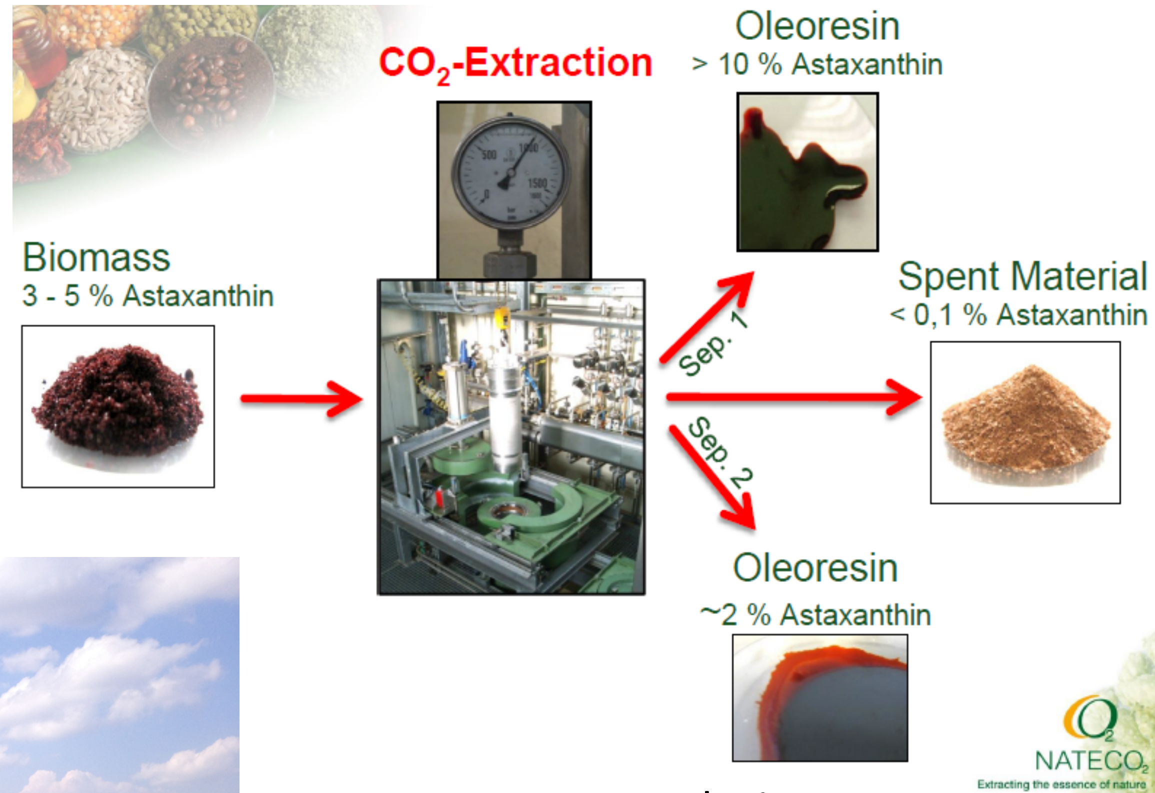


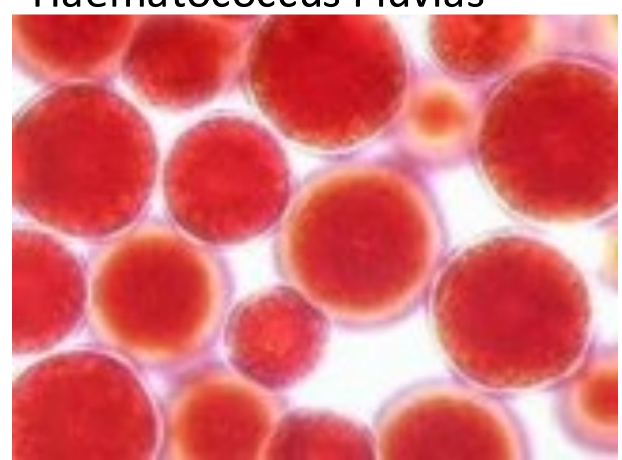
Figura 1. Estrutura química de alguns carotenóides.



ASTAXANTINA



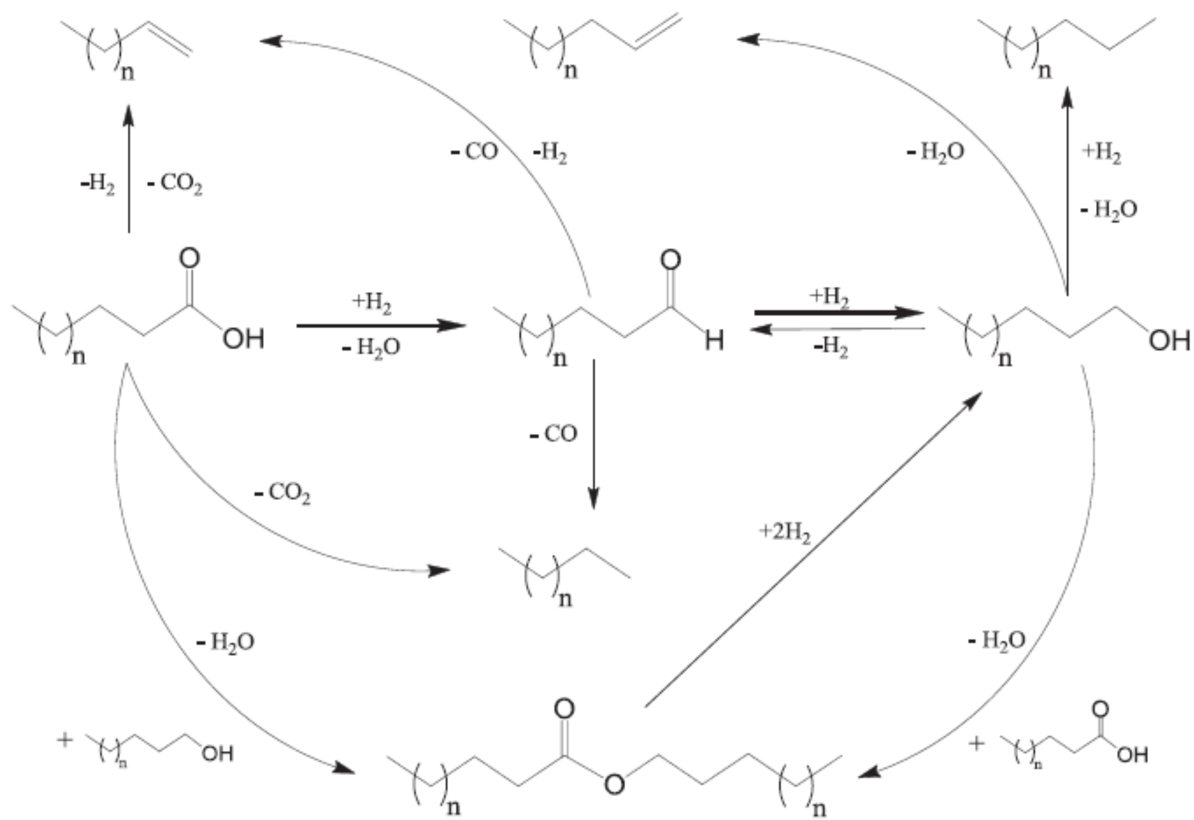
Haematococcus Pluvias



High Protein Concentration in Algae (More than 60%)

Hydrolized Algae Powder

Shrimp Farm



Scheme 1. Reaction pathways of stearic acid conversion over 4% ReO_x/TiO_2 catalyst.

Selective hydrogenation of fatty acids to alcohols over highly dispersed ReO_x/TiO_2 catalyst

Bartosz Rozmysłowicz [a], Alexey Kirilin [a,1], Atte Aho [a], Haresh Manyar [b], Christopher Hardacre [b], Johan Wärnå [a,c], Tapio Salmi [a], Dmitry Yu. Murzin [a,*]

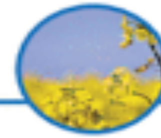
Journal of Catalysis 328 (2015) 197–207

PROCESSOS CATALÍTICOS EM ESCALA PILOTO

PROCAT
UNIDADE PROTÓTIPO
DE CATALISADORES

Processing microalgae: beyond lipids

Biofuels (2014) 5(1), 29–32



“A potential source of algae oil, important especially for Finland and the whole Baltic Sea region, could be surface aggregations of blue-green algae in the sea area.”

Dmitry Yu Murzin*[1], Päivi Mäki-Arvela[1] & Donato AG Aranda[2]

Keywords: carbohydrates ■ fractionation ■ fuels ■ lipids ■ microalgae ■ proteins

The utilization of renewable raw materials for production of diesel components is an important area, driven in part by regulations. For example, the EU aims to get 20% of its energy from renewable sources by 2020, including wind, solar and hydroelectric power, as well as geothermal energy and biomass.

According to the sustainable growth scenario, a significant part of the fossil fuel should be substituted by renewable sources, such as wood, grain and oilseeds [1]. However, the size of the plantations required for the current global world fuel consumption can significantly endanger food production. Therefore, conventional biofuel feedstocks are not totally suitable for implementation at a larger scale and new renewable sources are needed.

Recently, algae were proposed as promising renewable feedstock with evidential advantages over classical raw materials for fuel production [2–4]. The biomass yield from algae is five- to ten-times higher compared with land-based plants [1], reaching 10–25 g dry biomass per day per m^2 in open pond reactors [5] and 20–100 g per day per m^2 in closed photobioreactors [6]. Cultivation of algae can be done without competition with food production; that is, using nonarable land, and brackish or seawater.

A potential source of algae oil, important especially for Finland and the whole Baltic Sea region, could be surface aggregations of blue-green algae in the sea area. While such aggregations are still sparse in the western Gulf of Finland, they are extensive in the northern Baltic Proper and the Gulf of Bothnia. Such problematic aggregations also appear around the Åland archipelago. The total area covered by blue-green algae is currently above 350 thousand km^2.

Blue-green algae, like true algae, make up a portion of the phytoplankton in many water bodies. However, blue-green algae are generally not eaten by other aquatic organisms and, thus, are not an important part of the food chain, which is the opposite for true algae (e.g., green algae). Moreover, Baltic algae can grow at temperatures around 4°C, which can have significant importance if this technology is to be applied in Finland. The growth rate of blue-green algae in the Finnish Gulf could be 1–3 g dry biomass per day per m^2, giving algae with 10–15% lipid content (30% of which is polyunsaturated fatty acids). Rough estimations indicate that from the blue-green algae already present in the Baltic Sea, considering a surface biomass maximum of 60 g/m^2

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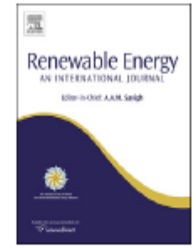

Glycerol conversion in the experimental study of catalytic hydrolysis of triglycerides for fatty acids production using Ni or Pd on Al_2O_3 or SiO_2

Gisel Chenard Díaz [a], Neyda de la C. Om Tapanes [a], Leôncio Diógenes T. Câmara [b,*], Donato A.G. Aranda [a]

$$TG + H2O \xrightarrow{\text{Catal. } \Delta} Gly + \underset{\text{(unsat.)}}{FFAs}$$

$$Gly \xrightarrow{\text{Catal. } \Delta} H2 + CO2$$

$$H2 + \underset{\text{(unsat.)}}{FFAs} \xrightarrow{\text{Catal. } \Delta} \underset{\text{(sat.)}}{FFAs}$$

Fig. 2. Steps in the hydrolysis reaction of triglyceride (TG).

Vol.3, No.7, 530-534 (2011)
http://dx.doi.org/10.4236/ns.2011.37074

Natural Science

Hydrolysis—Hydrogenation of soybean oil and tallow

Gisel Chenard Díaz[1], Rodolfo Salazar Perez[1], Neyda de la Caridad Om Tapanes[2], Donato Alexandre Gomes Aranda[1], Angel Almarales Arceo[1]

Catalysts

25% Ni/Al_2O_3, 5%Pd/Al_2O_3, 5%Pt/Nb_2O_5, 5%Re/Nb_2O_5

- [redacted]Al_2O_3 (Sasol, 160 m^2/g)
- Nb_2O_5 (CBMM, 80 m^2/g)
- $Ni(NO_3)_2$, $PdCl_2$, HReO4, H_2PtCl_6
- Wet Impregnation
- Calcination: 500 ^oC, 3h

25% Ni/Al_2O_3

- Pre-reduced at 400 C in H_2 for 2 h
- 10% catalyst (based on Algal oil)
- Algal Oil/Water 1:1 (wt)
- Temperature: 270 ^{o}C, P: 80 bar
- Time: 3h
- **Conversion: 95%**
- **Selectivity: 94% Saturated Fatty Acids (Lubricants)**

5% Pd/Al_2O_3

- Pre-reduced at 400 C in H2 for 2 h
- 10% catalyst (based on Algal oil)
- Algal Oil/Water 1:1 (wt)
- Temperature: 270 ^oC, P: 80 bar
- Time: 3h
- **Conversion: 95%**
- **Selectivity: 30% Saturated Fatty Acids**
- **64% Renewable Diesel**

5% Pt/Nb_2O_5

- **Pre-reduced at 300 °C** in H_2 for 2 h, Disp=42%
- 10% catalyst (based on Algal oil)
- Algal Oil/Water 1:1 (wt)
- Temperature: 270 °C, P: 80 bar
- Time: 3h
- **Conversion: 95%**
- **Selectivity: 30% Saturated Fatty Acids**
- **44% Renewable Diesel**
  - » **18% Fatty Alcohols**

5% Pt/Nb_2O_5

- Pre-reduced at 400 °C in H_2 for 2 h , Disp=18%
- 10% catalyst (based on Algal oil)
- Algal Oil/Water 1:1 (wt)
- Temperature: 270 °C, P: 80 bar
- Time: 3h
- **Conversion: 89%**
- **Selectivity: 19% Saturated Fatty Acids**
- **39% Renewable Diesel**
  - » **35% Fatty Alcohols**

5% Re/Nb_2O_5

- **Pre-reduced at 400 °C** in H_2 for 2 h , Disp=20%
- 10% catalyst (based on Algal oil)
- Algal Oil/Water 1:1 (wt)
- Temperature: 270 °C, P: 80 bar
- Time: 3h
- **Conversion: 90%**
- **Selectivity: 9% Renewable Diesel**
   » **91% Fatty Alcohols**

After Reaction

After Filtering

SUMMARY: HYDROLYSIS – HVO PROCESSES