



*Green aviation fuel: the future biofuel flagship*  
*Querosene de aviação como “carro-chefe”*  
*dos biocombustíveis do future*

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## ✓ Introduction / Motivation

## ✓ BioQAv production processes

- Towards new (oleochemistry)-based Biorefinery  
(Hydrolysis of Tryglicerides with Aqueous Phase Reforming)
- Biomass Gasification and Fischer-Tropsch Synthesis





# Introduction and Motivation

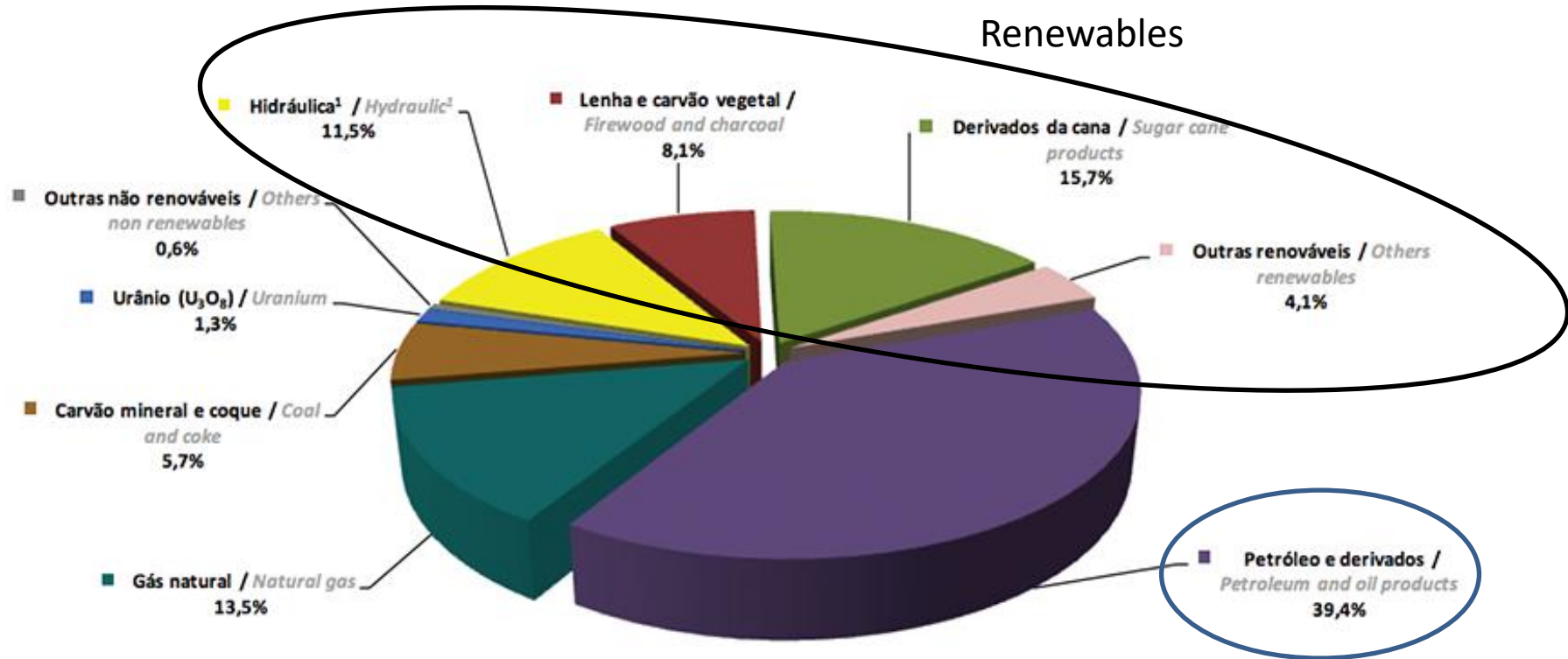


Figure : Brazil Energy Supply – 2016 (EPE)



# Introduction and Motivation

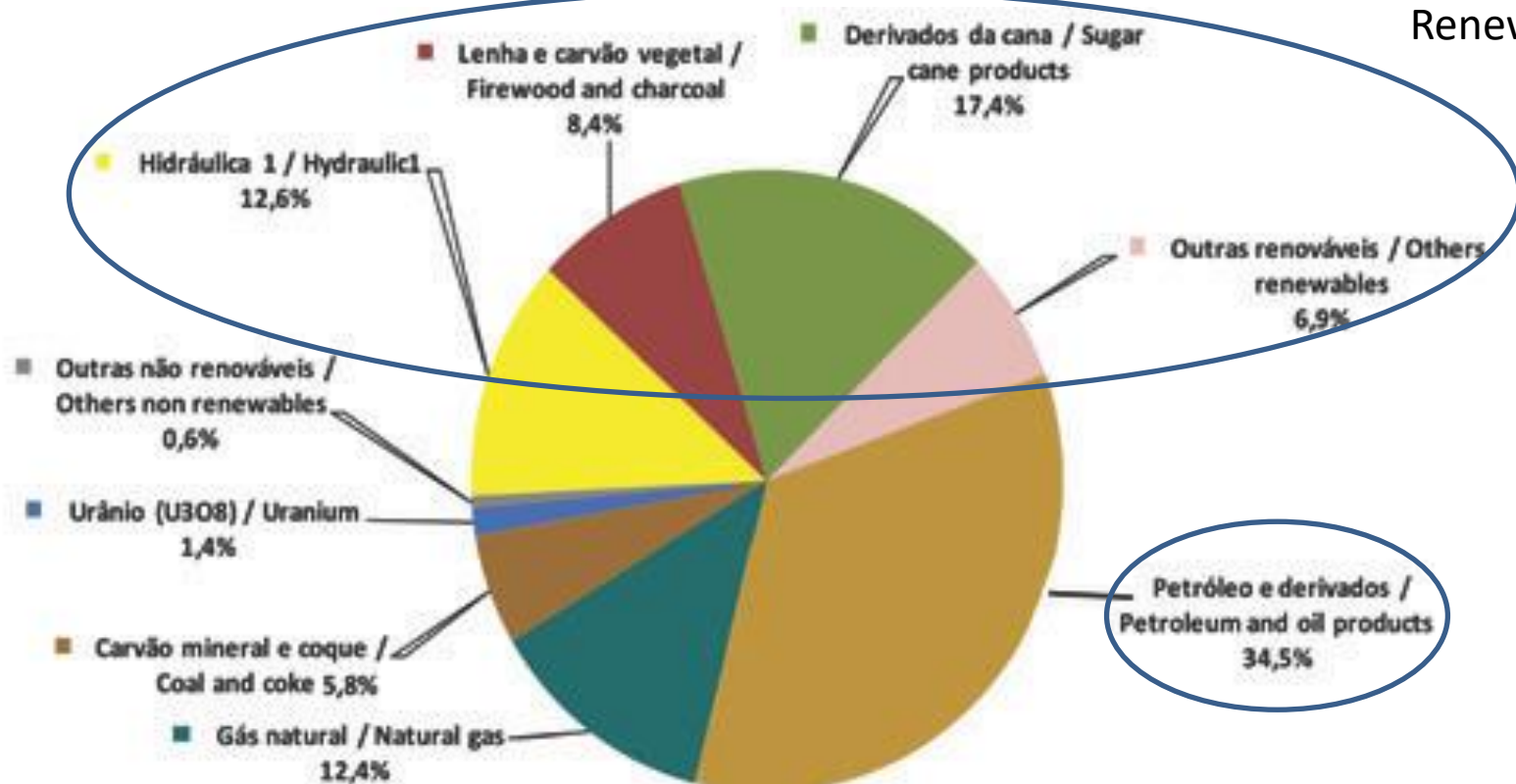
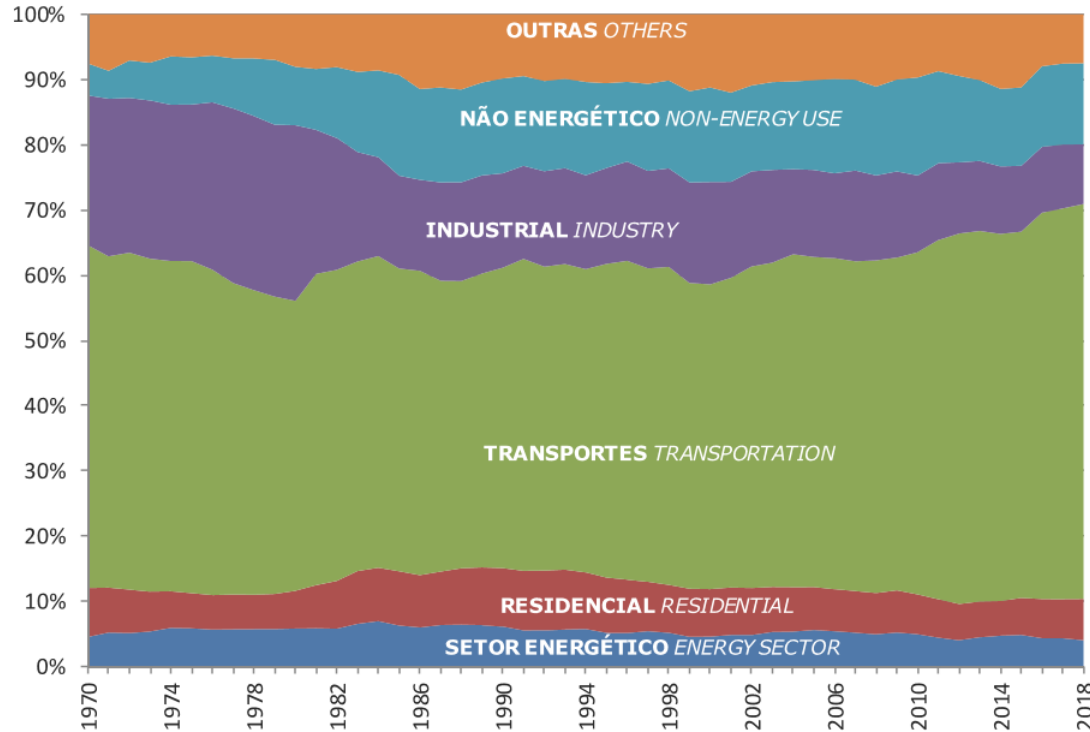


Figure : Brazil Energy Supply – 2019 (EPE)



## Composição Setorial do Consumo de Derivados de Petróleo (Oil Products Consumption by Sector)





# Introduction and Motivation

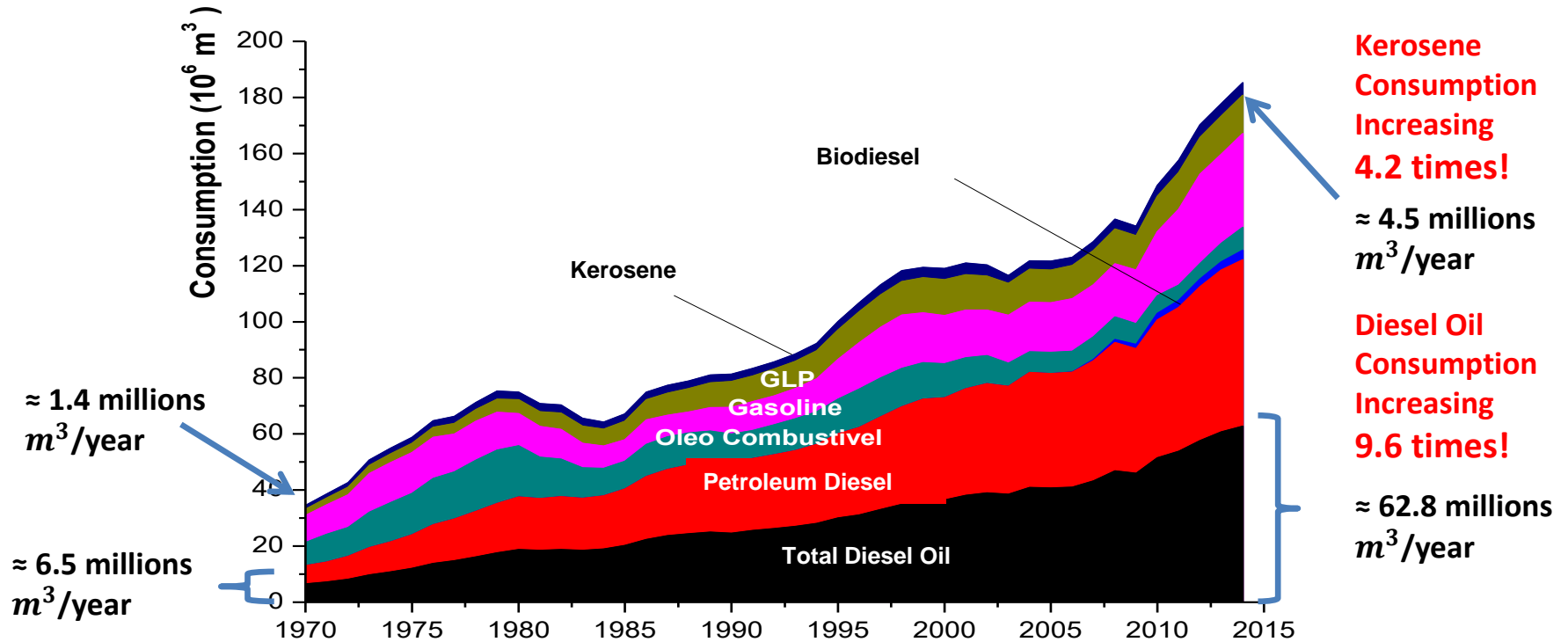


Figure 2: Brazil's petroleum-derived consumption evolution, 1970-2014.  
Source: EPE (2015).

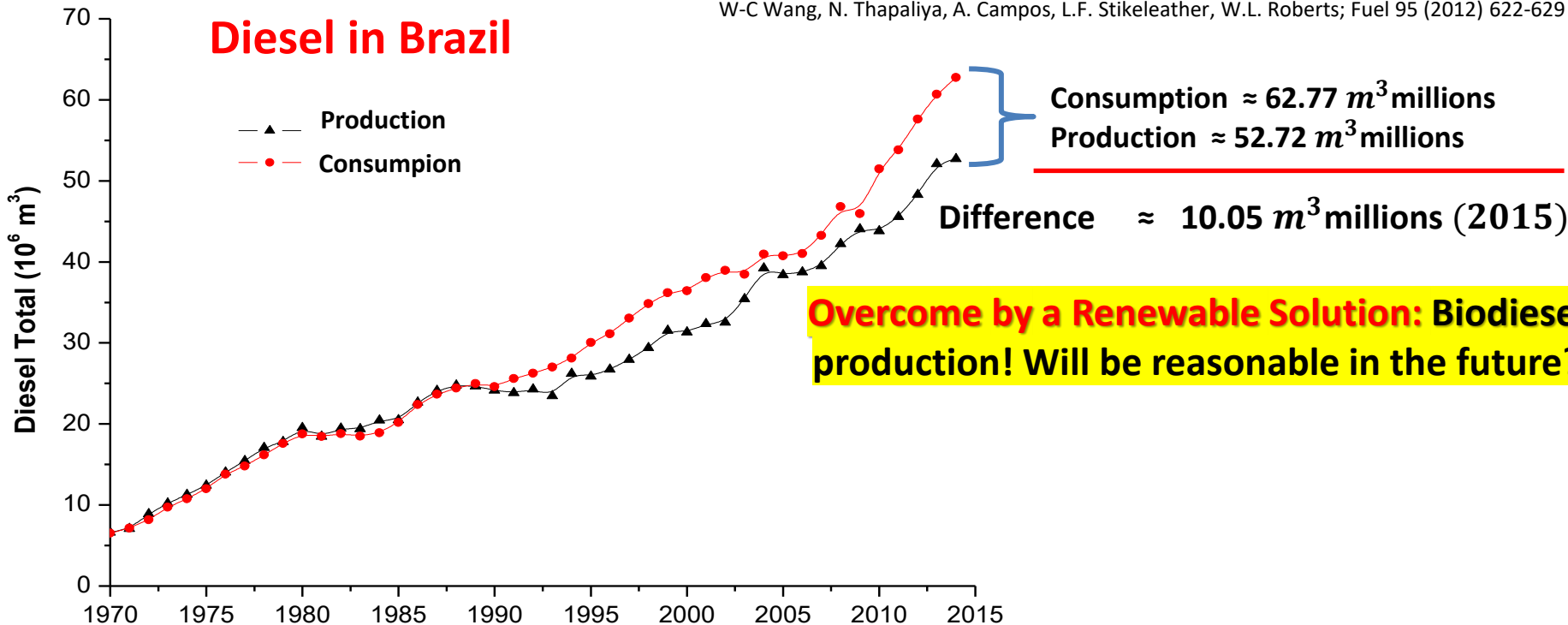


# Introduction and Motivation



T. Morgan, E. Santillan-Jimenez, A. E. Harman-Ware, Y. Ji, D. Grubb, M. Crocker; Chem. Eng. J. 189/190 (2012) 346-355

W-C Wang, N. Thapaliya, A. Campos, L.F. Stikeleather, W.L. Roberts; Fuel 95 (2012) 622-629



**Figure:** Diesel Consumption vs Production in Brazil, 1970-2014.

Source: EPE (2015).



T. Morgan, E. Santillan-Jimenez, A. E. Harman-Ware, Y. Ji, D. Grubb, M. Crocker; Chem. Eng. J. 189/190 (2012) 346-355

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### Diesel in Brazil

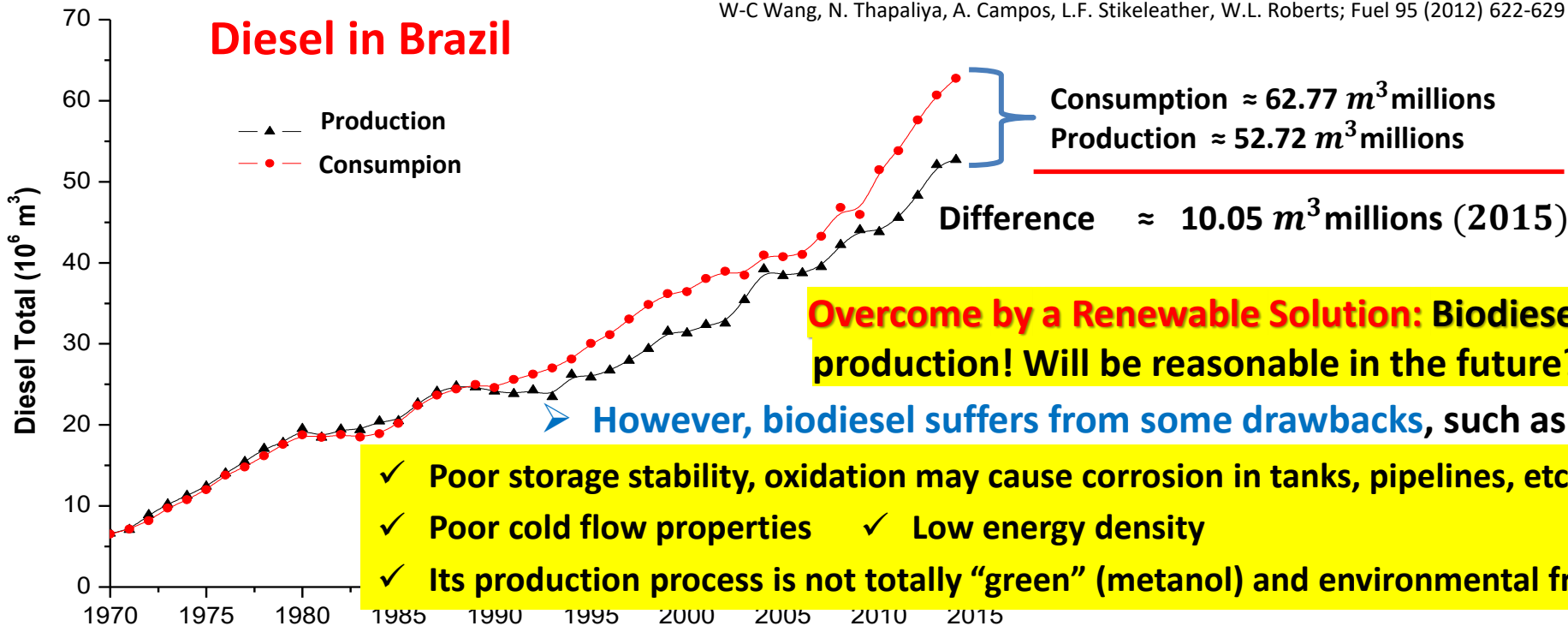


Figure: Diesel Consumption vs Production in Brazil, 1970-2014.

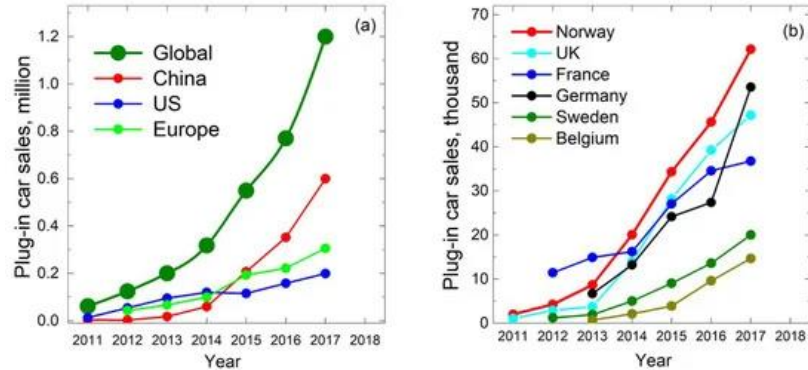
Source: EPE (2015).



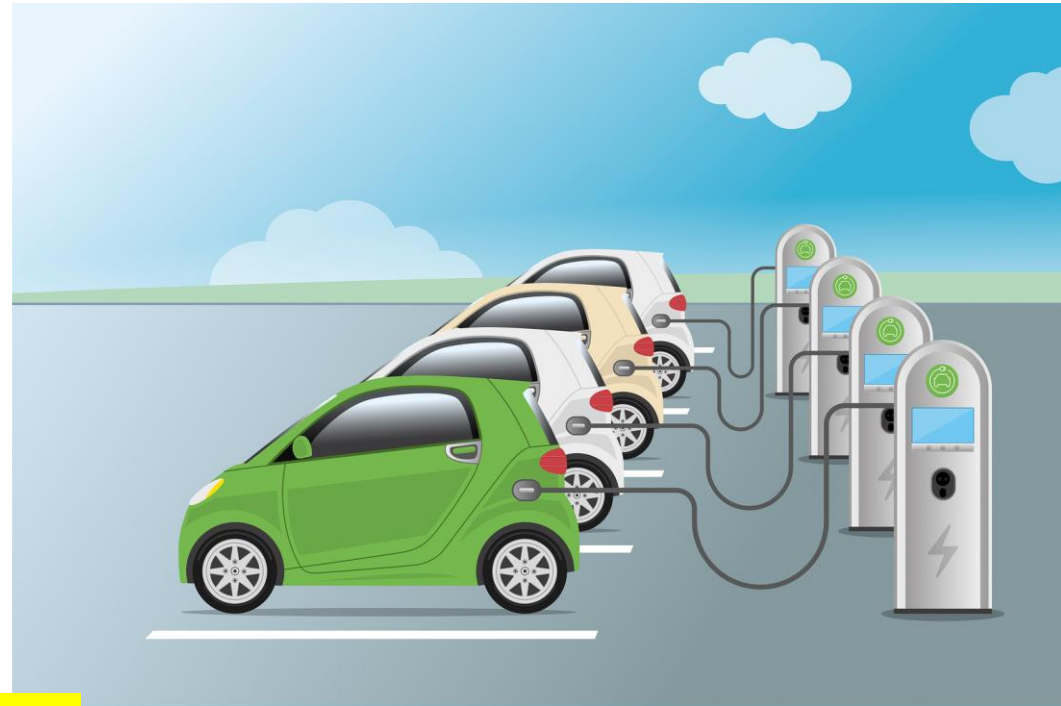


### Solution without CO<sub>2</sub> emission ?

### ✓ Electric vehicles



D.V. Pelegov and J. Pontes; Batteries 2018, 4(4), 65



**Mercado de carros elétricos no Brasil será de 180 mil unidades/ano em 2030 – EPE (JAC iEV40 – China – R\$ 67.000,0)**

### Future of Ethanol and Biodiesel Market ??



- **FLIGHTPATH TO AVIATION GREEN “FUEL” NOT INCLUDE ELECTRICITY !**
- **In the case of Jet Fuel, there is not still an equivalent “green” molecule, such as FAME, that can substitute or blend with traditional Kerosene.**
- **Airlines companies has set a target (2030) to replace part of the fossil Jet Fuel by renewable one. **By 2050: 50%****

**Then, there is a growing interest in the development of processes for the conversion of fats and oils, AND MAINLY LIGNOCELLULOSIC BIOMASS, into hydrocarbon fuels that can serve as drop-in replacements for petroleum-derived fuels**

**Therefore, biojet fuel will push biofuel production in the future**



# Why biojet fuels (BioQAv) ?

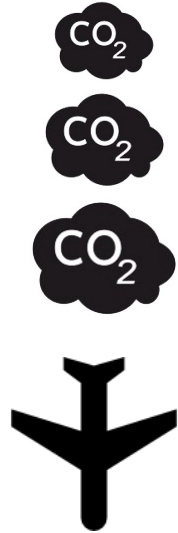
Aviation sector: 2% of global CO<sub>2</sub> emissions, with growth trend

## ICAO's CORSIA mechanism

<b>Until 2020</b>	Increasing the energy efficiency of the fleet in 1.5% per year	✓
<b>After 2020</b>	Stabilizing emissions through carbon neutral growth	⚠
<b>In 2050</b>	Cutting emissions in half in comparison to 2005 levels	⚠



**Aviation biofuel, biojet fuel, renewable kerosene...**



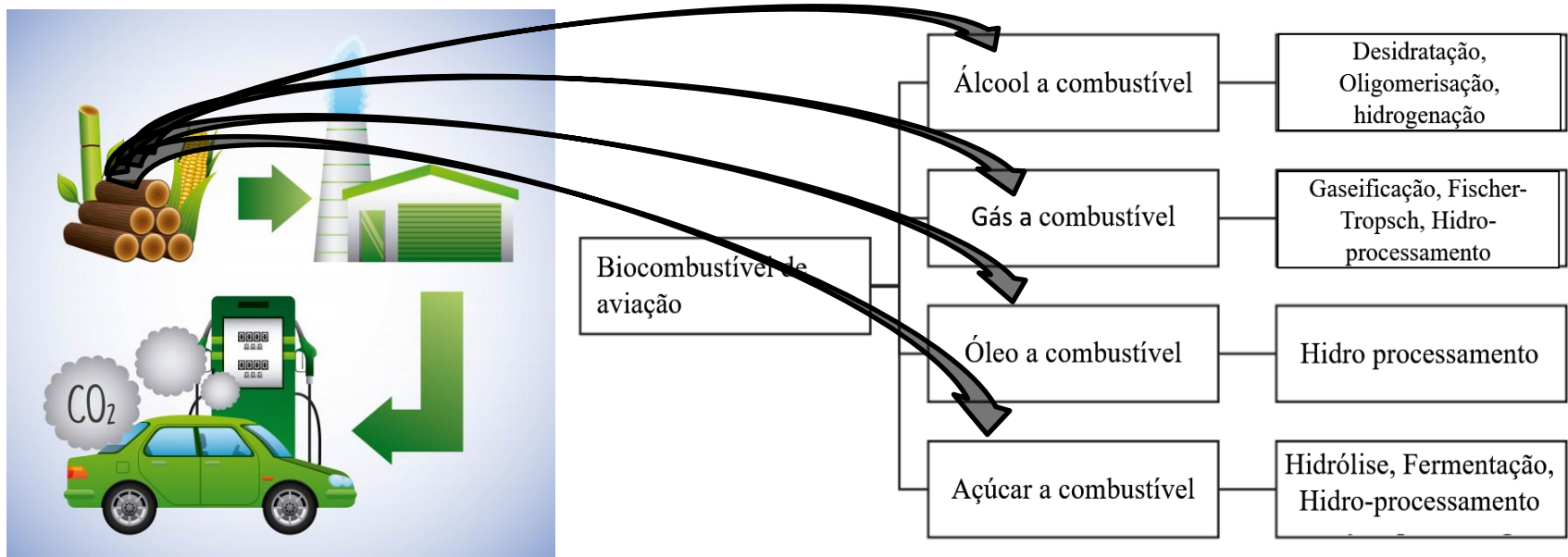


# ROTAS PARA PRODUÇÃO DE BIOQAV

- De álcool à BioQAv
- De açúcares a BioQAv
- De gás à BioQAv
- De óleo vegetal à BioQAv



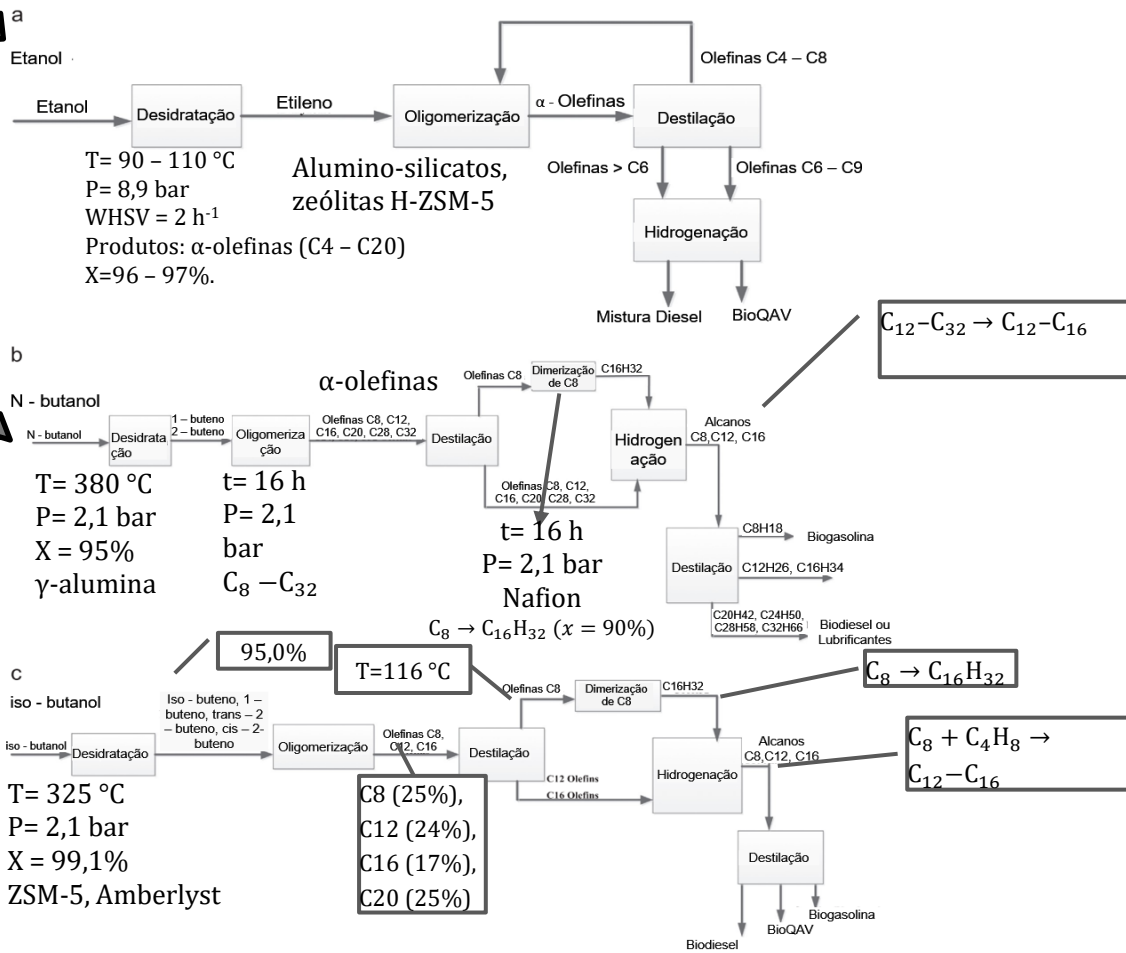
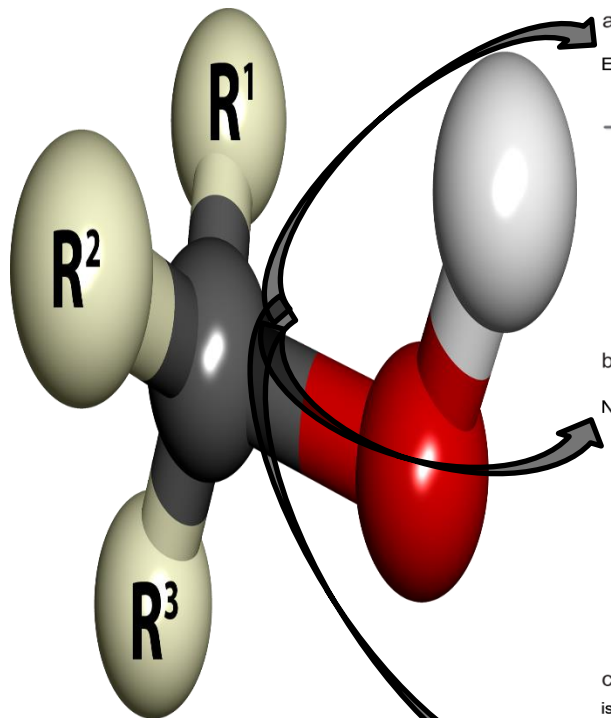
# Possíveis caminhos para conversão de biomassa à combustível de aviação (WHY, et al., 2019)



Rotas de produção de combustível de aviação aprovadas pela ASTM (CARVALHO, et al., 2019).

Rota de conversão	Abreviação	Conteúdo máximo de biocombustível	Ano de aprovação pela ASTM
Gaseificação e síntese de Fischer-Tropsch	FT	50%	2009
Hidroprocessamento de óleos vegetais	HEFA	50%	2011
Iso-parafias sintéticas	SIP	10%	2014
Kerosene parafínico sintetizado com aromáticos	SPK/A	50%	2015
Álcool para combustível de aviação	ATJ	50%	2018

# Álcoois a BioQAv (WANG, et al., 2016)

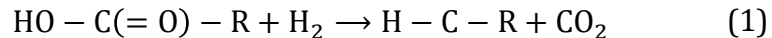


# Óleos Vegetais a BioQAv – HEFA (WHY, et al., 2019; WANG, et al., 2017)

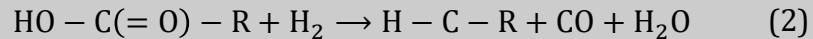


Rota de hidrocessamento para conversão de óleos vegetais em bioquerosene (WHY, et al., 2019)

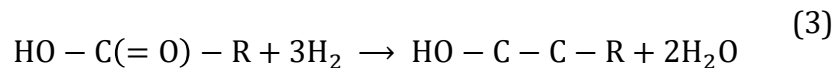
## Descarboxilação



## Decarbonilação



## Hidodesoxigenação

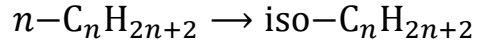


# Óleos Vegetais a BioQAv – HEFA (WHY, et al., 2019; WANG, et al., 2017)

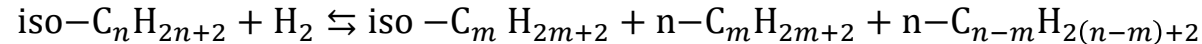


Rota de hidroprocessamento para conversão de óleos vegetais em bioquerosene (WHY, et al., 2019)

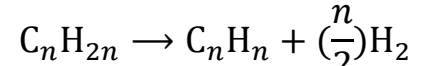
## Isomerização:



## Hidrocraqueamento:

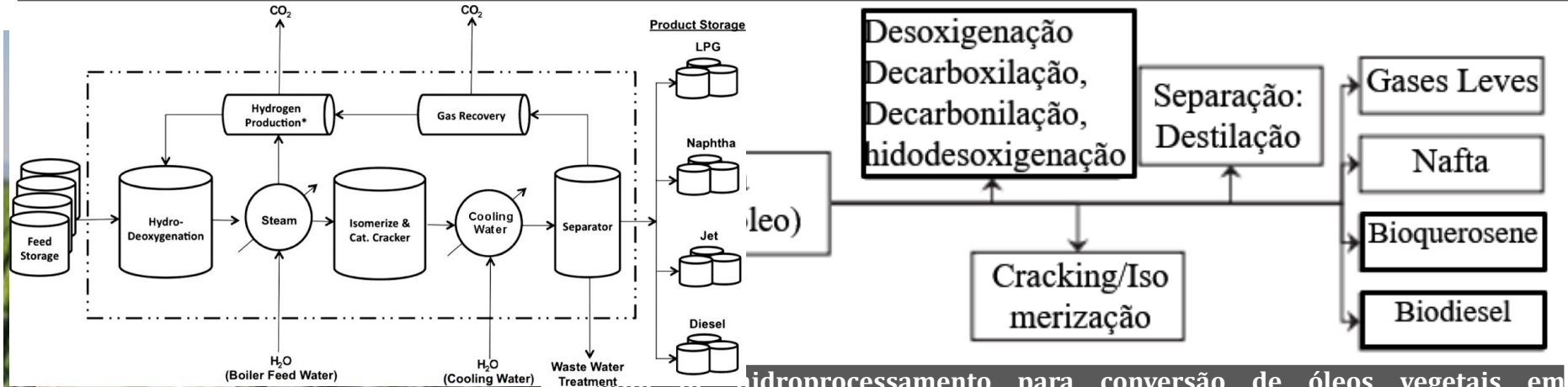


## Aromatização:





# Óleos Vegetais a BioQAv – HEFA (WHY, et al., 2019; WANG, et al., 2017)

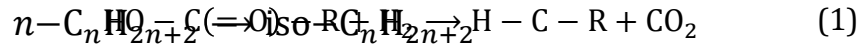


Processo de hidroprocessamento para conversão de óleos vegetais em bioquerosene (WHY, et al., 2019)



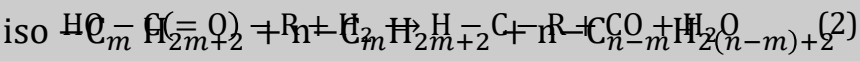
## Isomerização:

## Descarboxilação

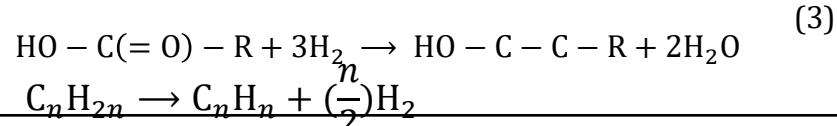


## Hidrocraqueamento:

## Descarbonilação



## Aromatização

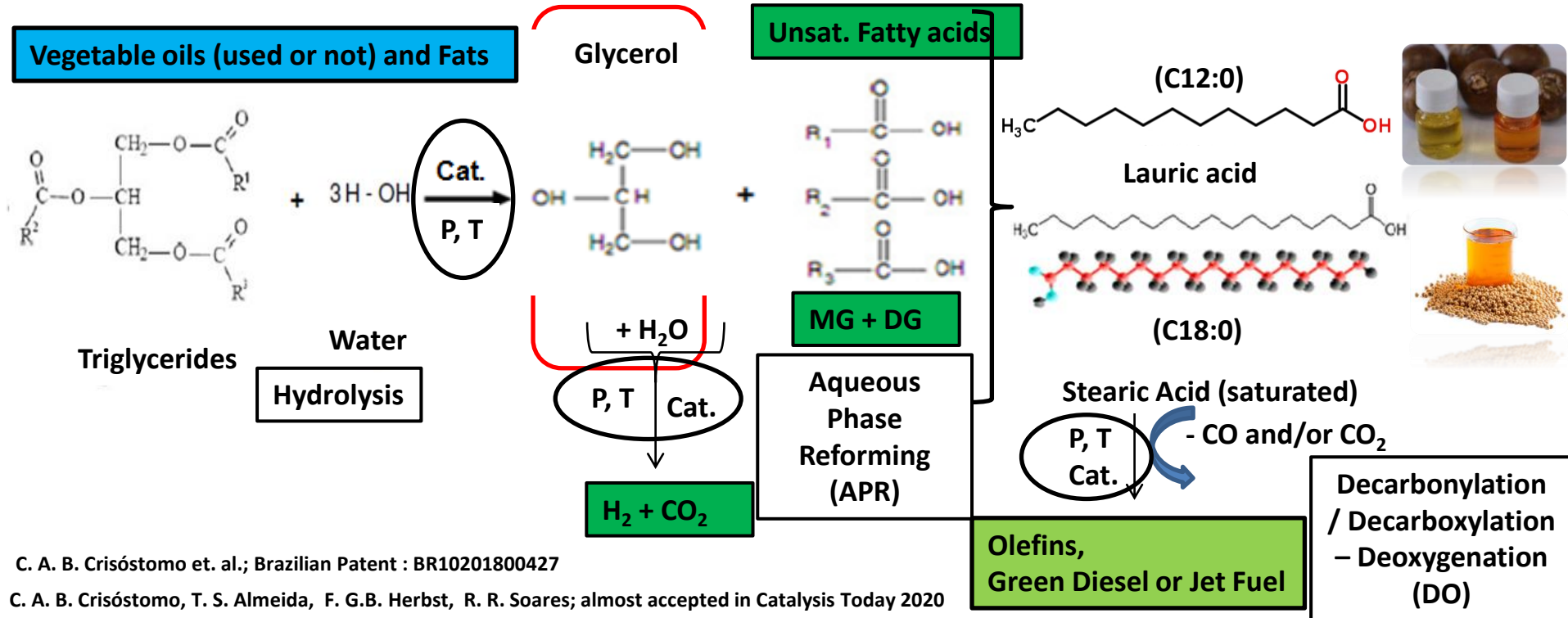


# Principais óleos Vegetais a BioQAv (WHY, et al., 2019)

Materia Prima	Rota de desoxigenação	Condições de reação	Catalisador	Rendimento de BioQAv (%)
Óleo de soja	Descarbonilação	T = 390 °C; P = 1 Mpa (H <sub>2</sub> ); τ = 8 h	Ni-MO/HY	48,2
	Hidrodesoxigenação	T = 370 - 385 °C; P = 3 Mpa (H <sub>2</sub> ); LHSV = 1 h <sup>-1</sup> ; H <sub>2</sub> /óleo = 800NL/L	Pt/Al <sub>2</sub> O <sub>3</sub> /Sapo-11	42 - 48
Resto de óleo de cozinha	Descarbonilação	T = 400 °C; P = 3 Mpa (H <sub>2</sub> ); τ = 8,0 h	Ni/Meso-Y	40,5
	Hidrodesoxigenação	T = 300 °C; P = 3 Mpa (H <sub>2</sub> ); τ = 7,5 h	Ni-Mo/γ-Al <sub>2</sub> O <sub>3</sub>	97
	Hidrodesoxigenação	T = 300 °C; P = 1 Mpa (H <sub>2</sub> ); GHSV = 2,33 min <sup>-1</sup>	Ni <sub>2</sub> P/AC	77,4 (biodiesel)
Óleo de mamona	Hidrodesoxigenação	T = 300 - 360 °C; P = 3 Mpa (H <sub>2</sub> ); WHSV = 2 h <sup>-1</sup>	NiAg/SAPO-11 ; Ni/USY-APTES-MCM-41	91,6; 80,3
Óleo de alga	Descarboxilação	T = 360 °C; Solvente = água; WHSV = 2 h <sup>-1</sup> ; τ = 45,0 min	Pt/C	90
Óleo de Macaúba	Descarboxilação	T = 300 °C; P = 1 MPa (H <sub>2</sub> ); τ = 5,0 h	Pd/C	85
Óleo de Palma	Hidrodesoxigenação	T = 300 °C; P = 1 MPa (H <sub>2</sub> ); τ = 5,0 h	Pd/C	82
	Hidrodesoxigenação	T = 330 °C; P = 5 MPa (H <sub>2</sub> ); τ = 5,0 h WHSV = 2 h <sup>-1</sup> ; $\frac{H_2}{\text{óleo}} = 800 \frac{\text{Ncm}^3}{\text{cm}^3}$	Ni-MoS <sub>2</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	58
Óleo de Jatrofa	Hidrodesoxigenação	T = 420 °C; P = 6 - 9 MPa (H <sub>2</sub> ); τ = 5,0 h LHSV = 0,5 - 2 h <sup>-1</sup> ; $\frac{H_2}{\text{óleo}} = 1500\text{NL/L}$	Ni-W/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	30
	Hidrodesoxigenação com H <sub>2</sub>	T = 300 °C; P = 4 MPa (H <sub>2</sub> ); LHSV = 1,33 h <sup>-1</sup>	WGS (Pt)/TiO <sub>2</sub>	75



## Towards new (oleochemistry)-based Biorefinery



C. A. B. Crisóstomo et. al.; Brazilian Patent : BR10201800427

C. A. B. Crisóstomo, T. S. Almeida, F. G.B. Herbst, R. R. Soares; almost accepted in Catalysis Today 2020

G.C. Diaz, R.S. Perez, N.C.O. Tapanes, D.A.G Aranda; *Natural Science* 3 (2011) 530-534

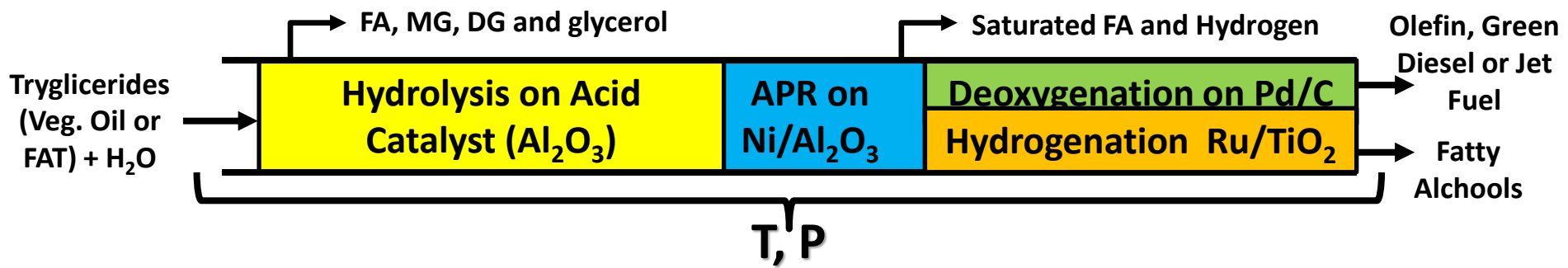
T.J. Logan, D.C. Underwood, T.C. Rheinecker; USPTO 4,218,386 -1980

G.W. Huber, J.W. Shabaker, J.A. Dumesic; *Science* 300 (2003) 2075-2077

S.A.W. Hollak, M.A. Ariens, K.P. de Jong, D.S.van Es; *ChemSusChem*. 2014, 7, 1057-1060



## Towards new (oleochemistry)-based Biorefinery





Biomassa à BioQAv = Gaseificação + SFT

**BIOVALUE E META ESPECÍFICA:**

**Estudar Sistema Integrado (FT + SIP + SPK/A)  
para produção de BioQAv (BTL)**

- Síntese de Fischer-Tropsch (FT)
- Síntese de Iso-Parafinas (SIP)
- Síntese de Querosenes Parafínicos c/ Aromáticos (SPK/A)



*Whole chain decentralized biomass valorization to advanced biofuels:  
development and assessment of thermochemical routes integrated to biomass  
production and biochemical routes*

## Brazil – EC coordinated call on Advanced Lignocellulosic Biofuels

HORIZON 2020 (H2020)

Work Programme 2016-2017 - ‘Secure, Clean and Efficient Energy’

LCE-22-2016: International Cooperation with Brazil  
on Advanced Lignocellulosic Biofuels - BECOOL

European Commission (EC) and MCTIC/CONFAP/FAPESP

## State Research Foundations – Technical and Financial Support



## Companies – Technical and Financial Support

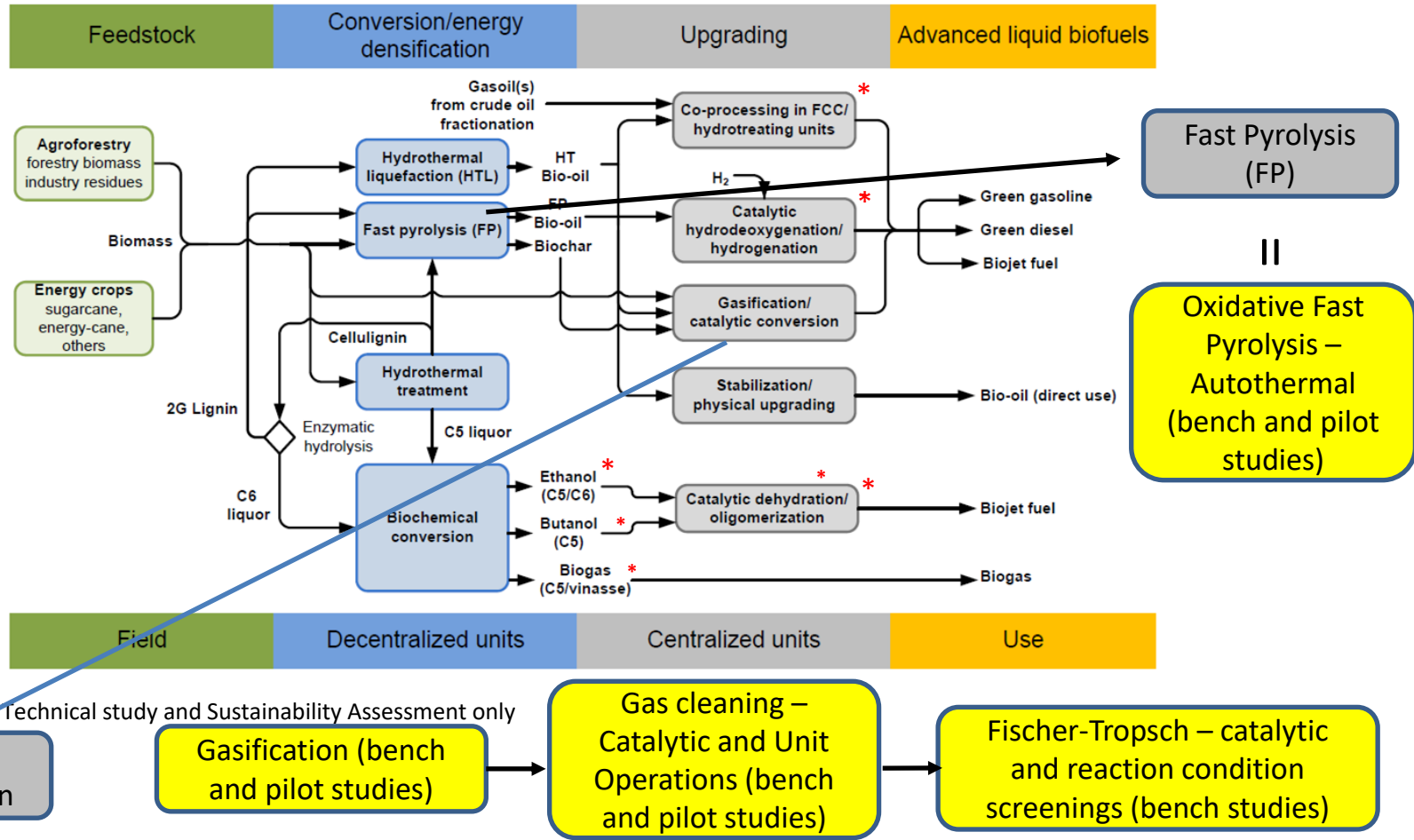


## Research Institutions – Technical Execution



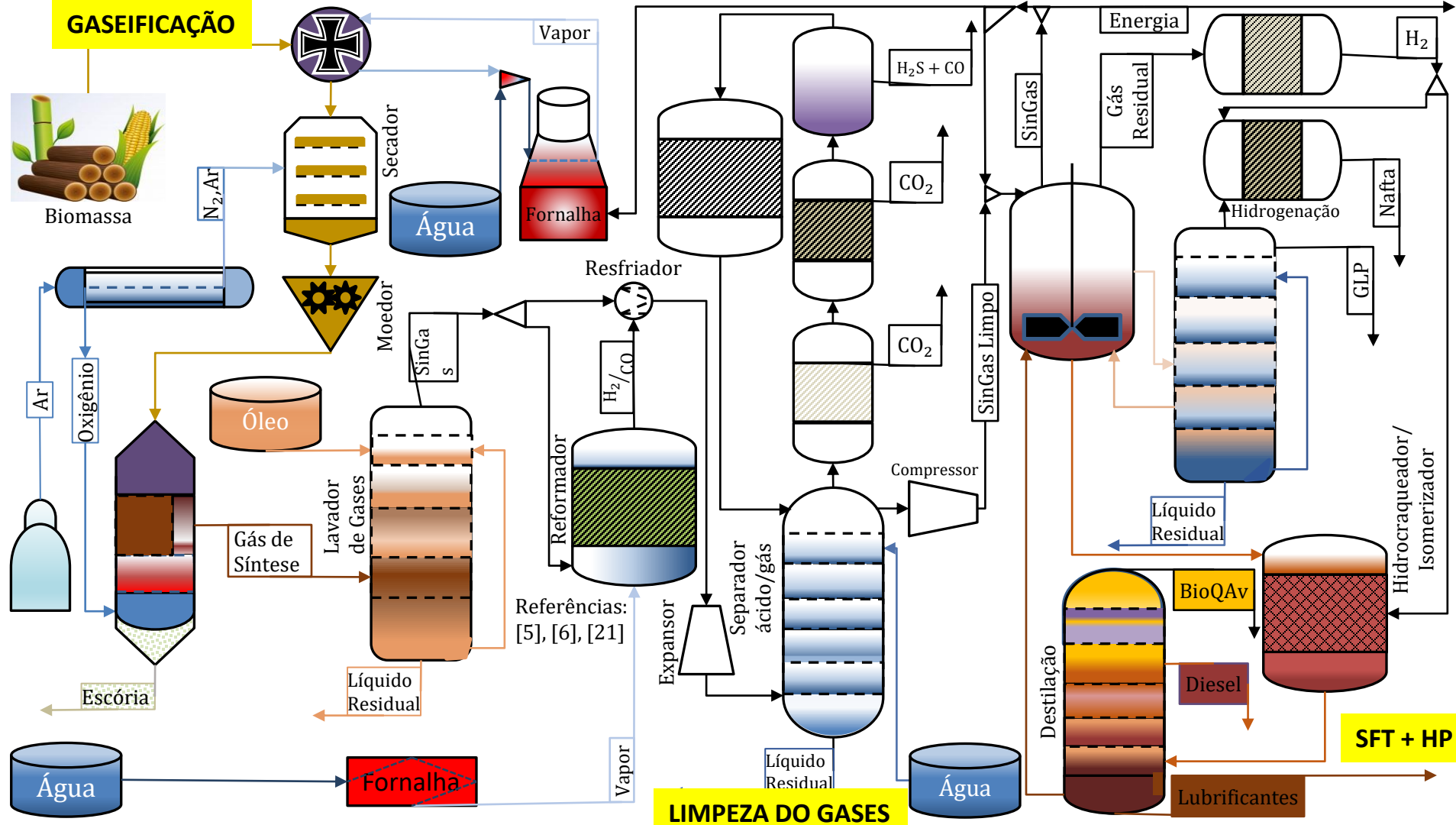
# GENERAL

# GOALS

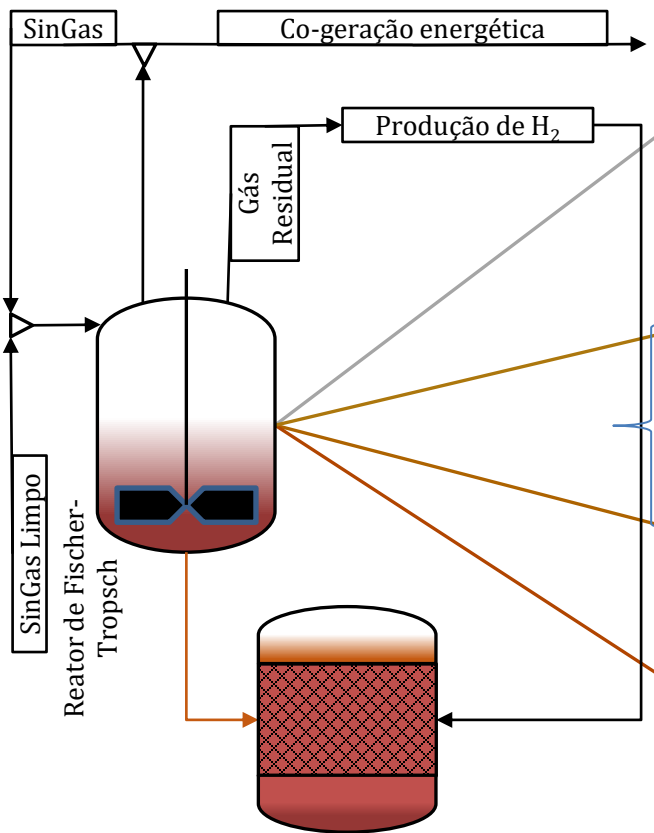




# GASEIFICAÇÃO

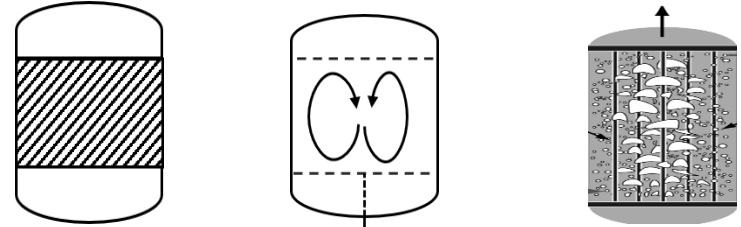


# Estudo do Processo de Fischer-Tropsch Integrado

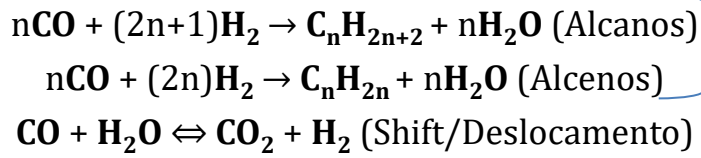


**Hidroprocessamento:**  
Craqueamento/Isomerização/Ciclização/Aromatização

## PRINCIPAIS REATORES



## PRINCIPAIS REAÇÕES (Cat. c/ Fe)



GRAU DE POLIMERIZAÇÃO:  
Distribuição Anderson-Schulz-Flory (ASF)

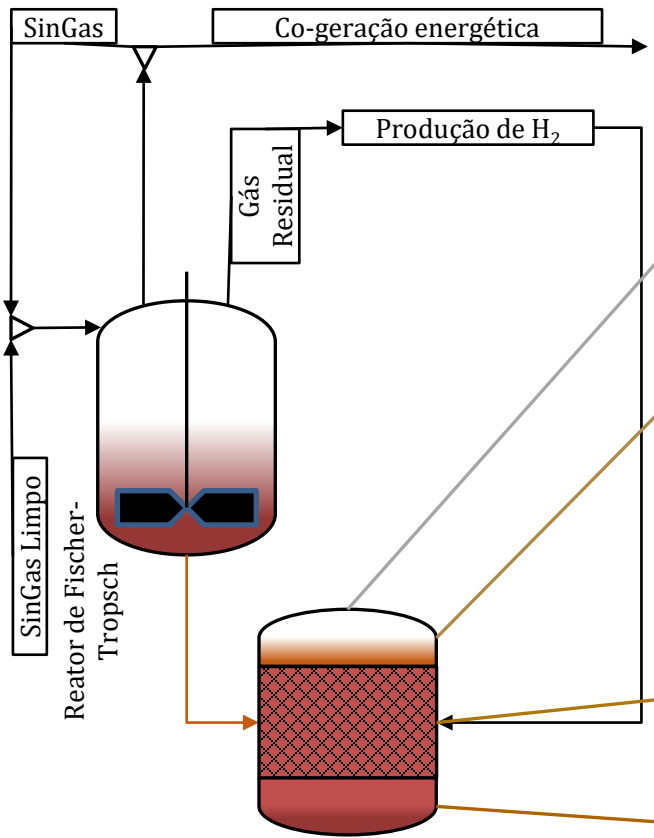
## CONDIÇÕES REACIONAIS

Pressão: 10 – 30 atm  
Temperaturas: 180 – 250 °C

## PRINCIPAIS CATALISADORES

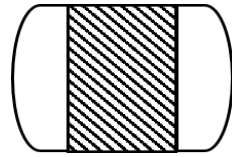
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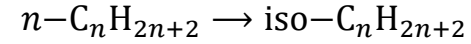
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## PRINCIPAIS REATORES

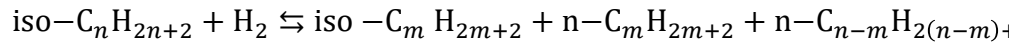


## PRINCIPAIS REAÇÕES

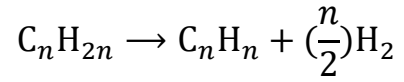
Isomerização:



Hidrocraqueamento:



Aromatização:



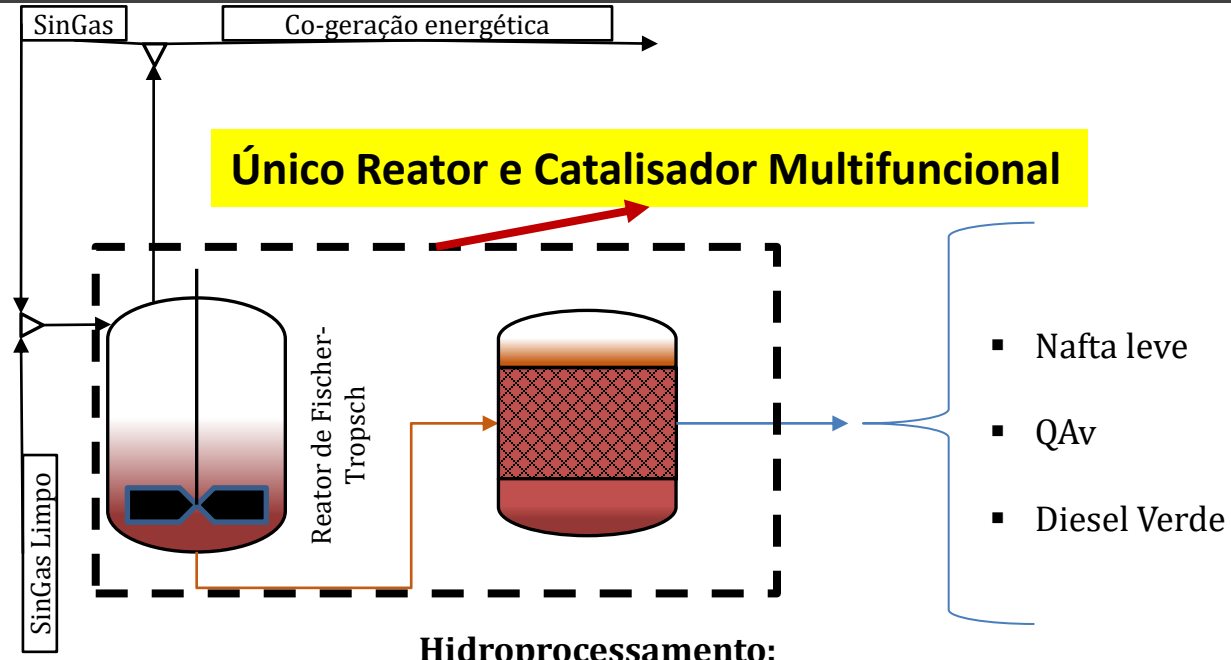
## CONDIÇÕES REACIONAIS

$T = 230 - 400 \text{ }^\circ\text{C}$   
 $P = 5 - 10 \text{ bar}$

## PRINCIPAIS CATALISADORES

Ni, Pt, Ni  
Suportados em Zeólitas, Alumina, Sólidos ácidos (ou misturados)

# Estudo do Processo de Fischer-Tropsch Integrado



## OBJETIVOS

- ESTUDAR TERMODINÂMICA DOS PROCESSOS E SINTETIZAR CATALISADORES VISANDO OTIMIZAR CONDIÇÕES REACIONAIS IGUAIS (T E P) PARA OPERAÇÃO EM SÉRIE.
- OTIMIZAR QAv
- LEVANTAR CINÉTICA DA SFT

**OBRIGADO PELA ATENÇÃO!  
DÚVIDAS ?**

**➤ INTEGRAR OS PROCESSOS DE HIDROPROCESSAMENTO E FISCHER-TROPSCH NUM SÓ.**

Agradecimentos: ao Engo. Délio Barroso de Souza pela elaboração de vários slides