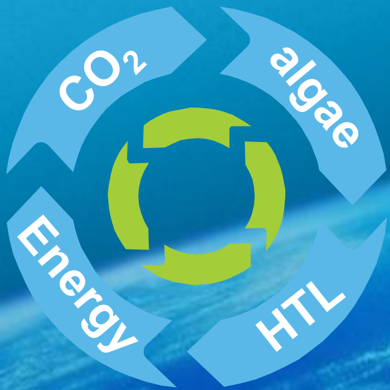
# Hydrothermal processing of microalgae





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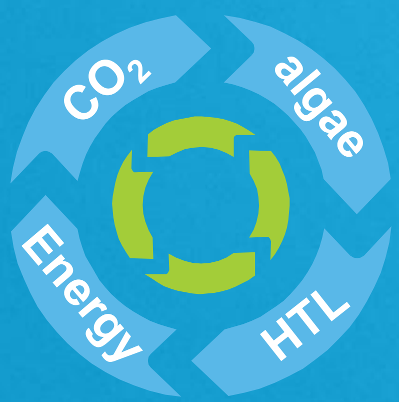
## Challenges of our time

- Increasing population
  *with increasing needs*
- Energy supply
- Water and Food
- Climate Change




## BIOFUELS – Incentives for use of Algae

130 g $CO_2$ /km [443/2009] (2015)

↓

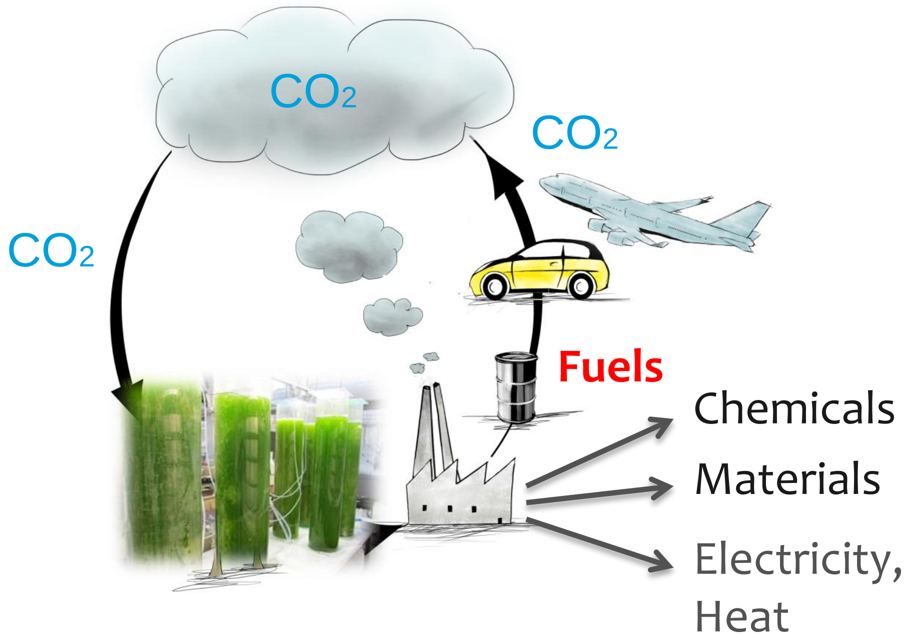
70 g $CO_2$ /km (2025)

**EC**: clear market incentives for algal biofuels
by counting algae fuels <u>quadruple</u> (4x)

[amendment COM(2012) 595, of the EU- Directive 98/70/EC w.r.t. EU mandatory biofuels targets]

# Energy & Chemicals from Microalgae

CAN MICRO ALGAE REALLY HAVE AN IMPACT ?




- Food and Fuel
- High valuables
- Carbon Footprint
- Security of supply

Energy use: 550 EJ worldwide
including 200 EJ oil (87 Mbbl/d)
of which 20 EJ chem./mat.

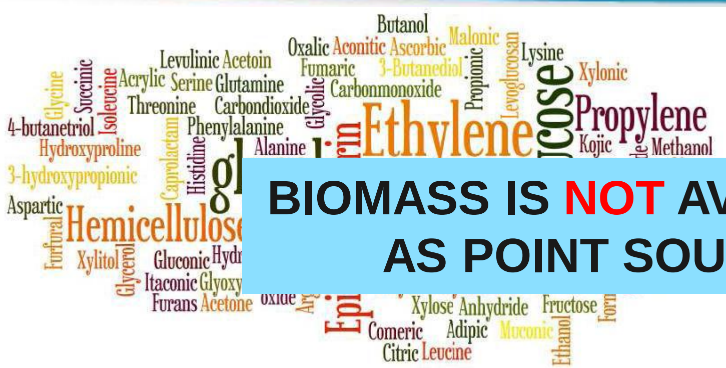
Biomass potential ?
world grain production = 2300 Mta
(3-5 t/ha yr) ≈ 20 EJ

With microalgae on same area:
(> 40 t/ha yr) > 400 EJ
($400\ 10^6$ ha)

**Microalgae do have the potential to contribute significantly to renewable transportation fuels and chemicals**

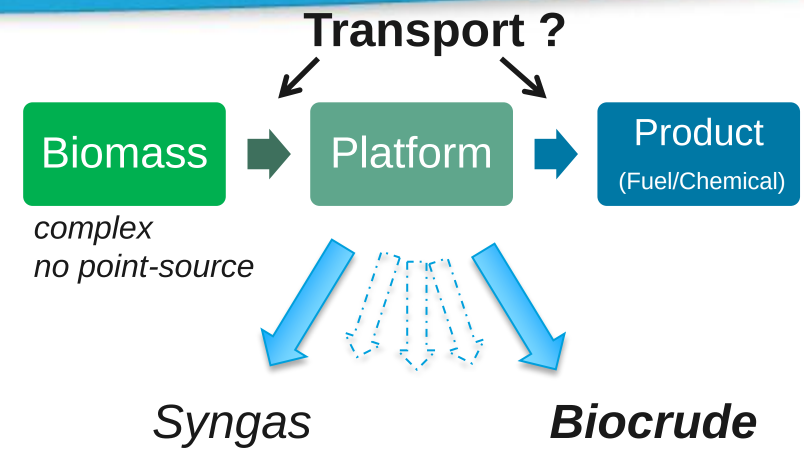
# Biomass and Biorefinery: biocrude

**VALORISATION OF BIOMASS; ECONOMY OF SCALE;**




**BIOMASS IS NOT AVAILABLE AS POINT SOURCE**

IEA Bioenergy – Task 42



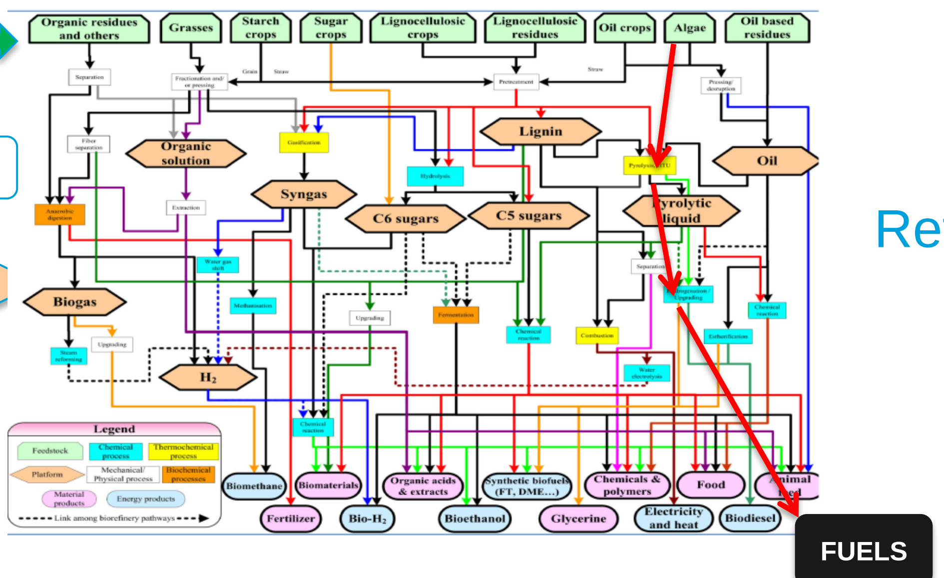

biomass

Processes

&

'Platforms'

Products




*Biocrude*

**Economy of Scale**

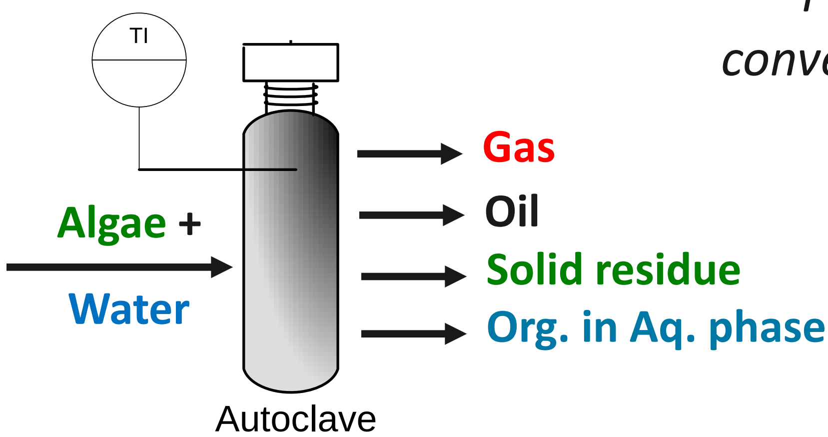
Refinery: > 75,000 bbl/day

> 4,000 kta

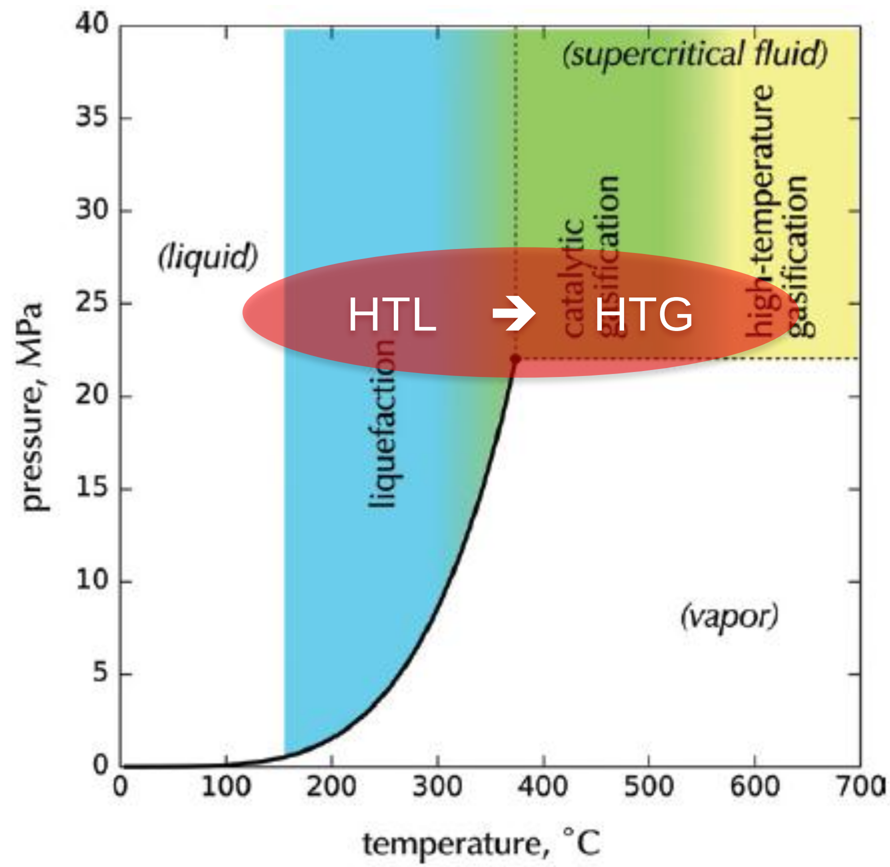
> 100,000 ha algae

Transport !

# Hydrothermal Conversion of Micro Algae



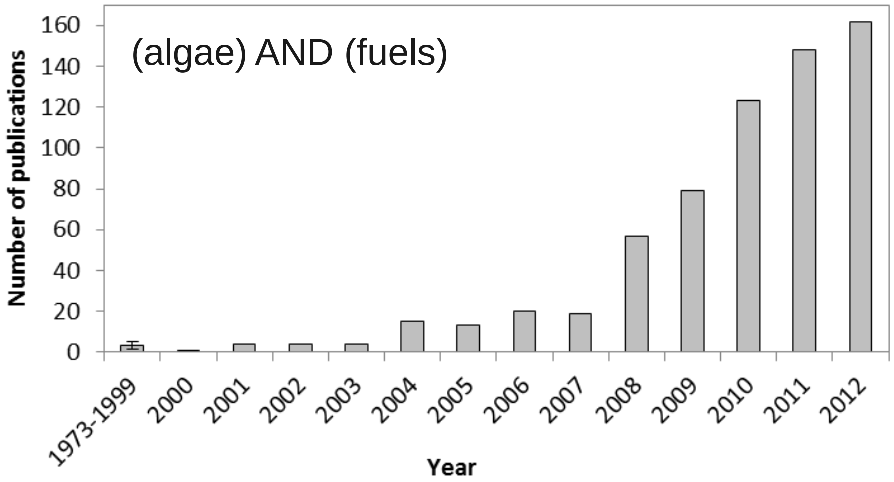

*Process is which complex organic material is converted at **elevated pressure and temperature** in crude oil and chemicals*



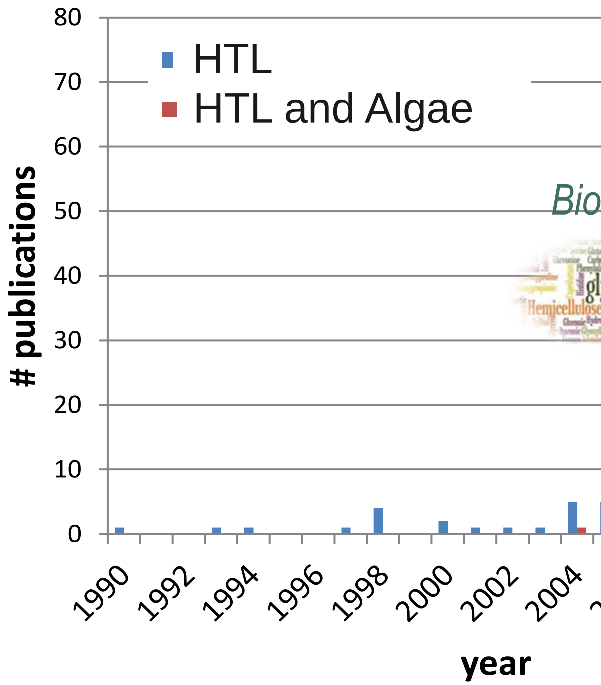

**Why Hydrothermal Conversion ?**

* water properties change drastically
- from polar → apolar solvent
- dissociation constant ↑↑

* many biomass streams are "wet"
* seen as robust technology




## **TRENDS** in Fuels from Algae …




(Web of Science, 11/11/2013)

Fraction HTL in Algae to Fuels studies increases …

*… not without reason !*

**Algae to Fuels via HTL is relative new development; HTL not only for algae**

# Algae to Fuels and Chemicals

Liquefaction for …

- Transport (densification)
- Economy of Scale
  (existing infrastructure)
- Separating minerals
- …

**Fuels & Lipids**

*Requires 'wet extraction' technologies*

- lipids
- protein
- carbohydrates
- other (VAP)

Feed, Food (chemicals) …

P,T ↑

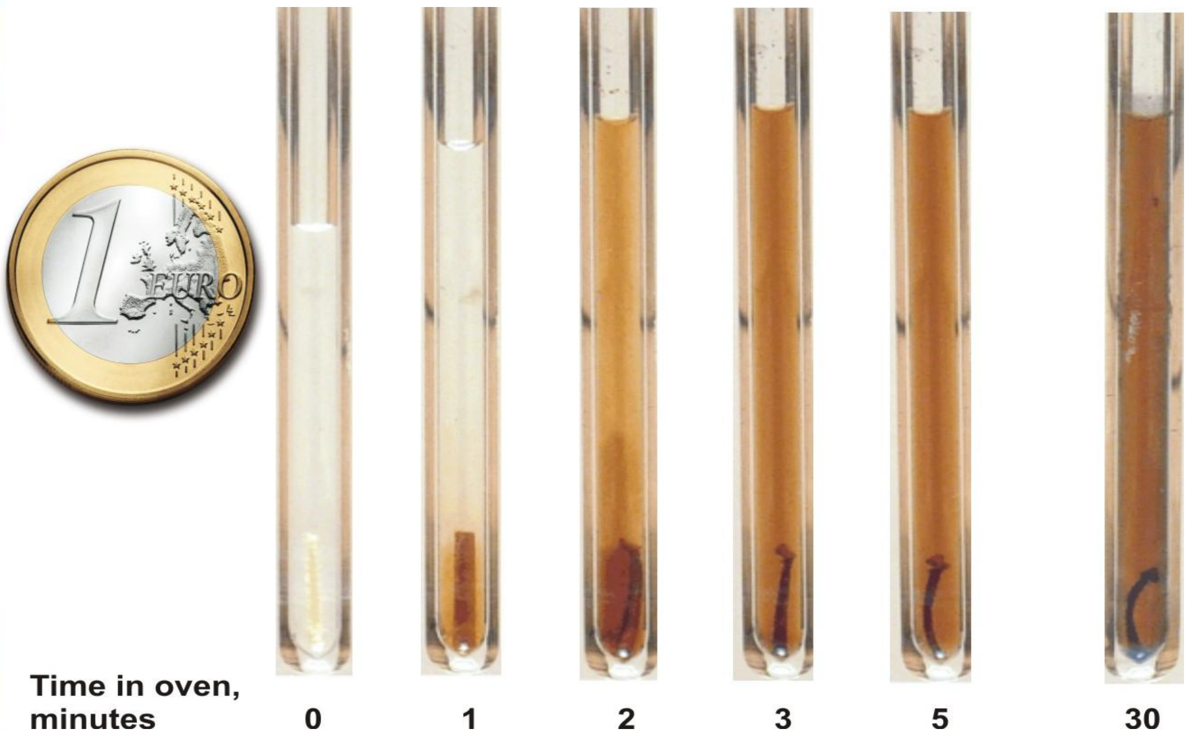
Biocrude as 'platform' for transport

# Contents



**Can we 'fast track' HTL of microalgae by learning from early HTL work ?**

# HYDROTHERMAL LIQUEFACTION




300 °C

*Knezevic, thesis U.Twente (NL)*

Initial focus: liquefying dry, lignocellulosic material
(pine wood, poplar, bagasse, …)

Development was stopped in piloting phase:
too many operational issues + poor economics

# Contents

- HTL – Introduction
- History

Critical Issues:

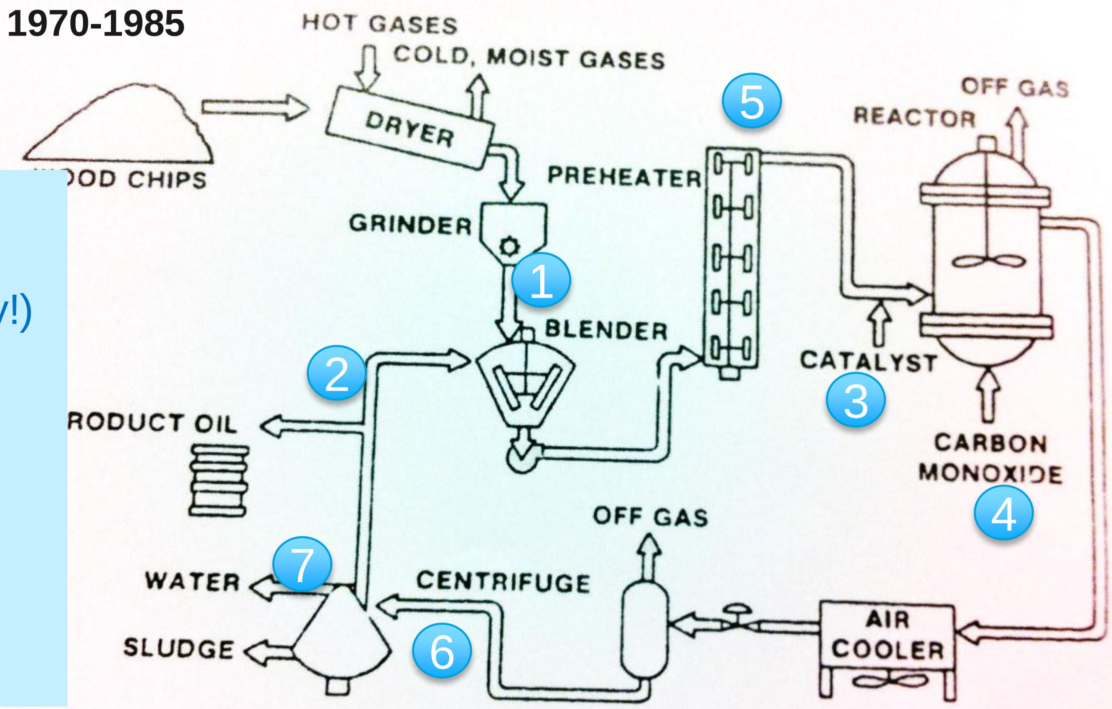
1. Pressurizing slurries (30wt%)
2. Accumulation 'heavies' (viscosity!)
3. Catalyst => salts
4. $CO, H_2$ added (3-6 wt%)
5. Scraped heater (fouling !)
6. Phase separation
7. Water effluent quality
8. Mechanical issues
9. Economics

**Can we 'fast track' HTL of microalgae by learning from early HTL work ?**

# HYDROTHERMAL LIQUEFACTION

*PERC process ('70-ies; 5-9 kg/h), pilot scale in Albany (USA; '80-ies; design: 3 t/d)*

**+/- 1970-1985**




Initial focus: liquefying dry, lignocellulosic material (pine wood, poplar, bagasse, …)

Development was stopped in piloting phase: too many operational issues + poor economics

# HTL of micro algae biomass

HTL of biomass

- before 1990: focus dry, lignocellulosic biomass
- fundamentals and technology aspects not fully understood
- around year 2000: “stranded in pilot scale phase” (PERC / LBL / HTU® / …)

  *[technology, economics + attractive alternative for dry biomass: pyrolysis]*

## Can HTL be more successful for microalgae ?

- Logical step: wet biomass → wet conversion technology
- Easy to pressurize; non-fibrous, no grinding needed, pumpable,
- Less lignin & (hemi)cellulose;
- **Keep it simple**: no co-solvents, no catalyst, no CO gas, …
- **process integration** benefits for up- and downstream processes

**R&D** **(2008 - …)** oil yield and composition (P, T, algae composition, etc.)
Reaction fundamentals
Scale-up (continuous operation, phase sepn., heat exchange)

# Contents



# HTL of microalgae

- Small scale, batch experiments (autoclaves)
  - Proof of concept
  - Optimization process conditions (P,T,..)
  - Reaction fundamentals
  - Oil analysis and processing
- Process Evaluation & integration
- Continuous operation
  - Optimization process conditions
  - pumping, heat exchange, phase separation, …
- Large scale piloting & commercialisation

# Contents



# HTL of microalgae

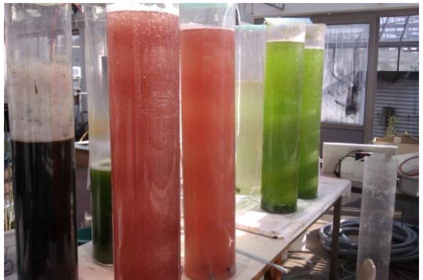
## Process Conditions

- Algae species
- Solvent
- Catalyst
- Pressure
- Temperature
- Residence time
- Heating rate dT/dt (↑↓)
- Reducing gases
- …

## Output

- Product distribution (oil/gas/aq. phase/solid )
- Composition
- Energy Recovery
- C recovery in oil
- N content in oil
- N recycling

Different algae species

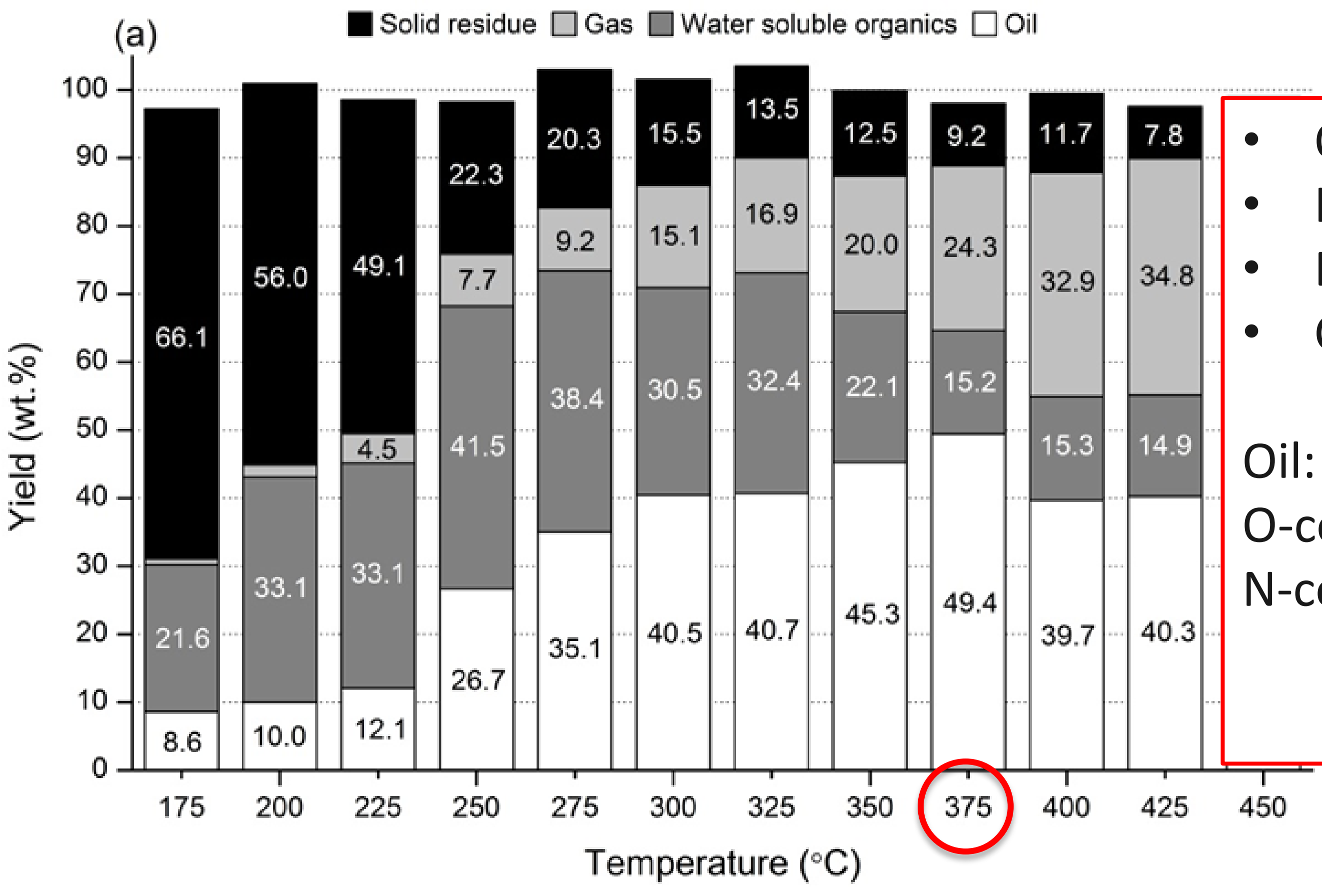


## *presented results based on : Desmodesmus sp.*


ingrepro

*fresh water strain;*
*low lipid (10%), high protein (50%)*
*carbohydrates (20%)*

# HTL … Effect of temperature (1)




- Oil yield: 49 wt%
- HHV: 36 MJ/kg,
- Energy yield 75% (as oil)
- C-recovery: 72%

Oil:

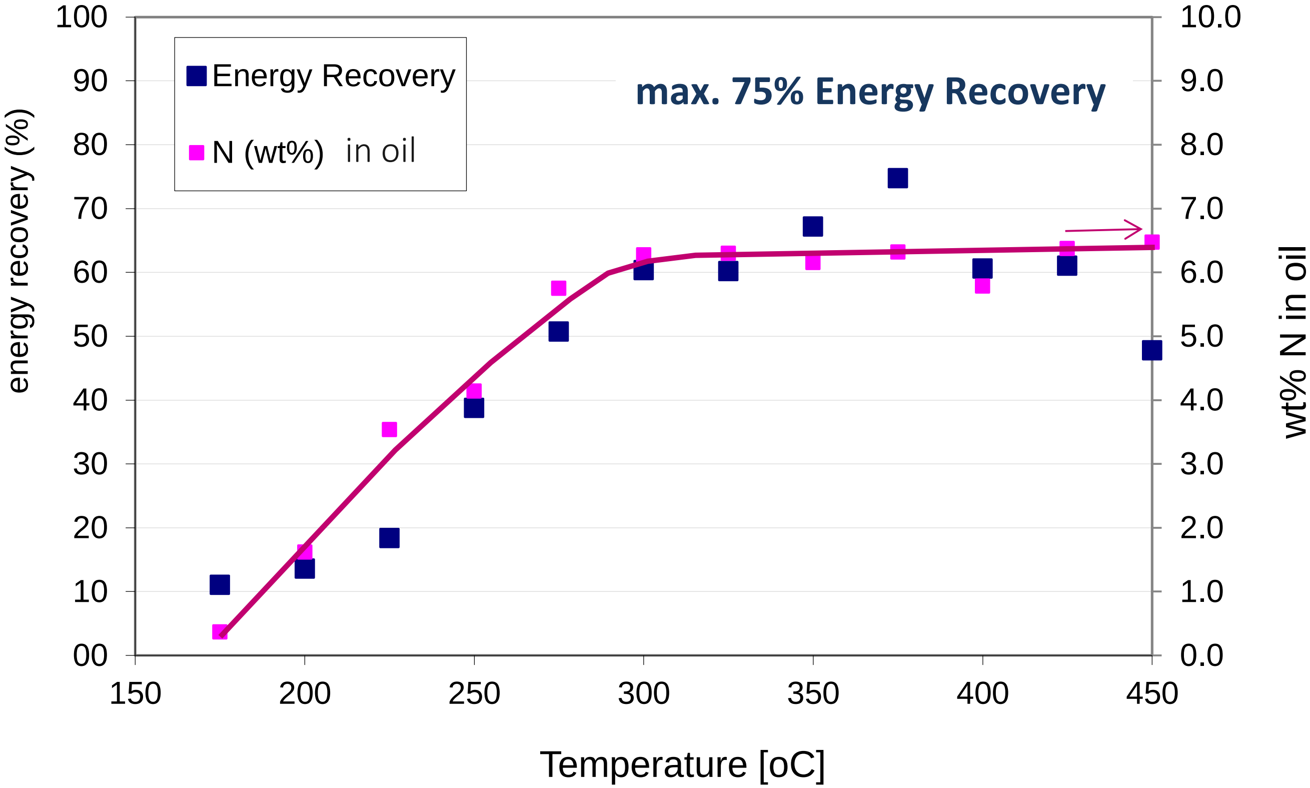
O-content: 10 wt%

N-content: 5.8 wt%

(algae: 6.8 wt%)

(Garcia-Alba et al, 2012)

# Oil yield and Elemental Composition



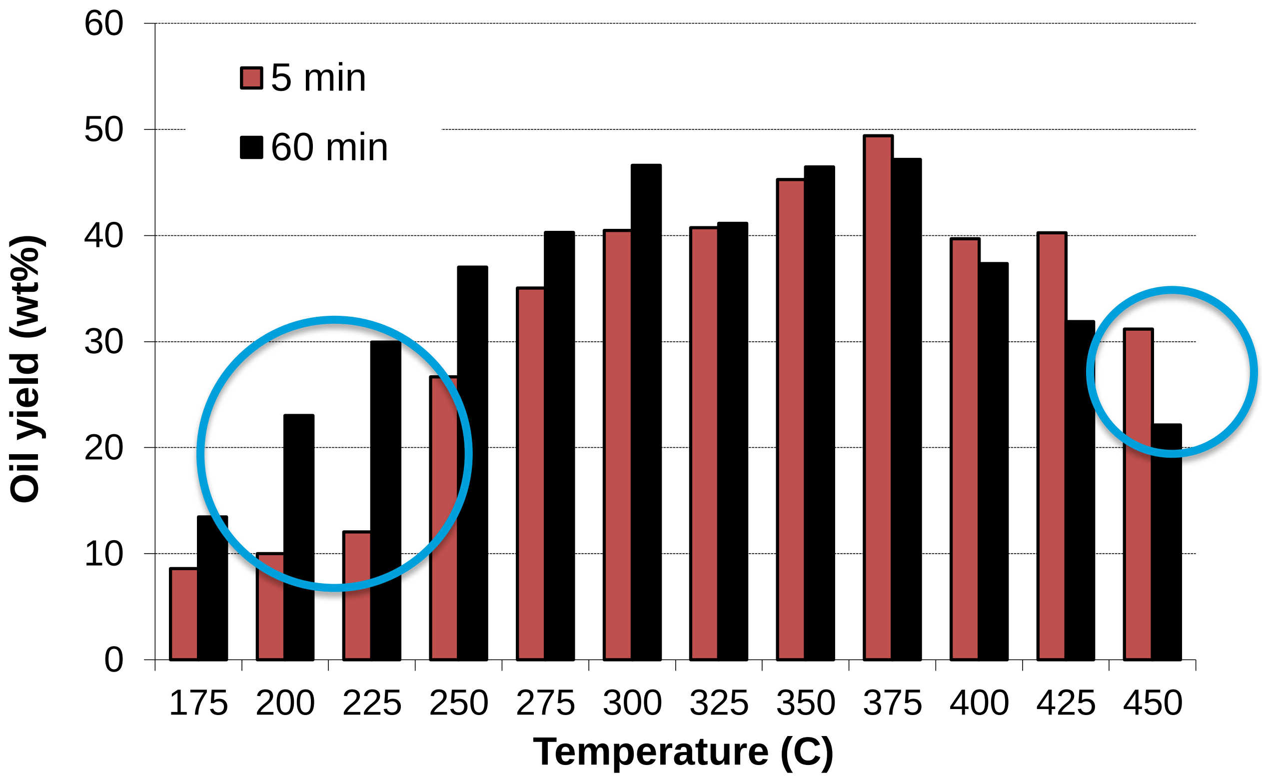

N content increases with oil yield and Energy recovery

O content in oil decreases from 26 wt% at 175°C to 10 wt% above 350°C √

**N-content is too high and must be reduced**

**Preferrably, N is recovered and recycled to cultivation**

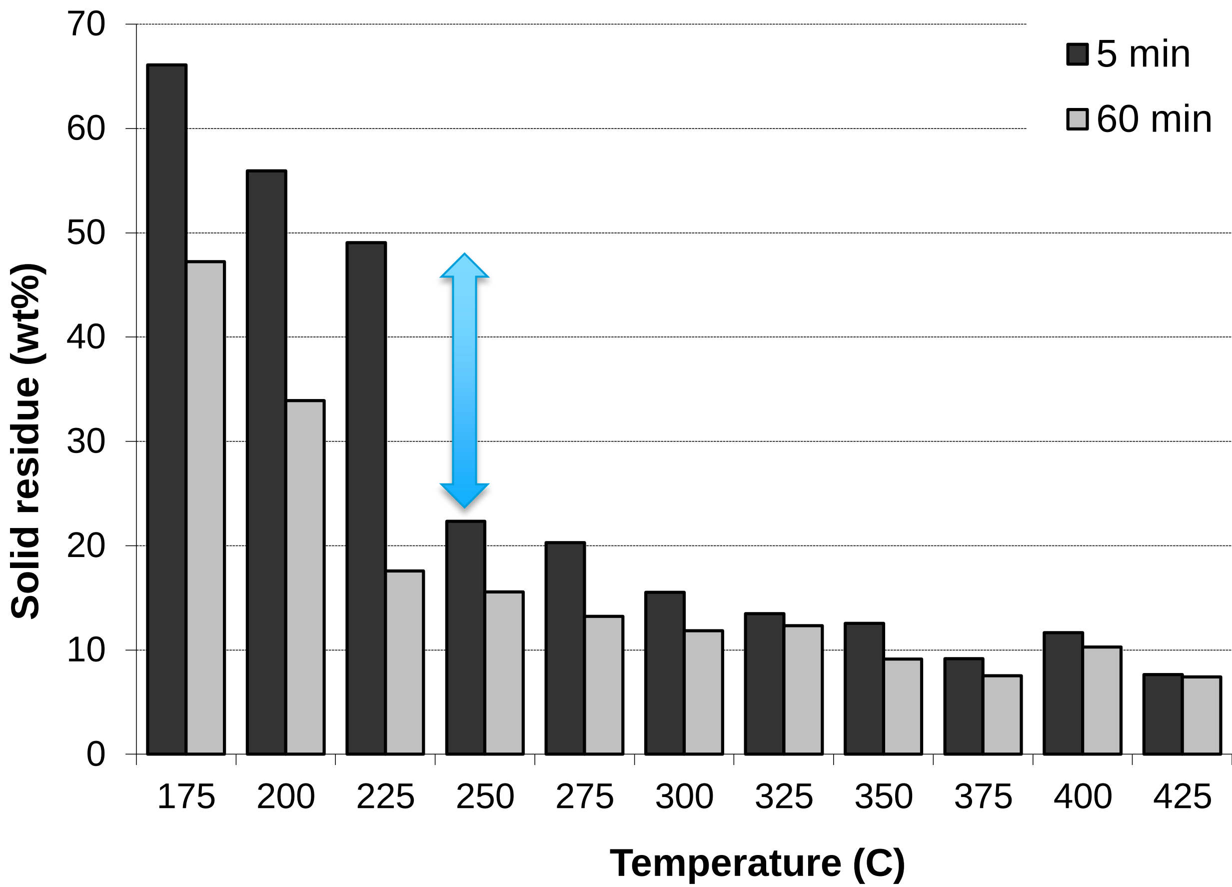
# HTL … Effect of process time

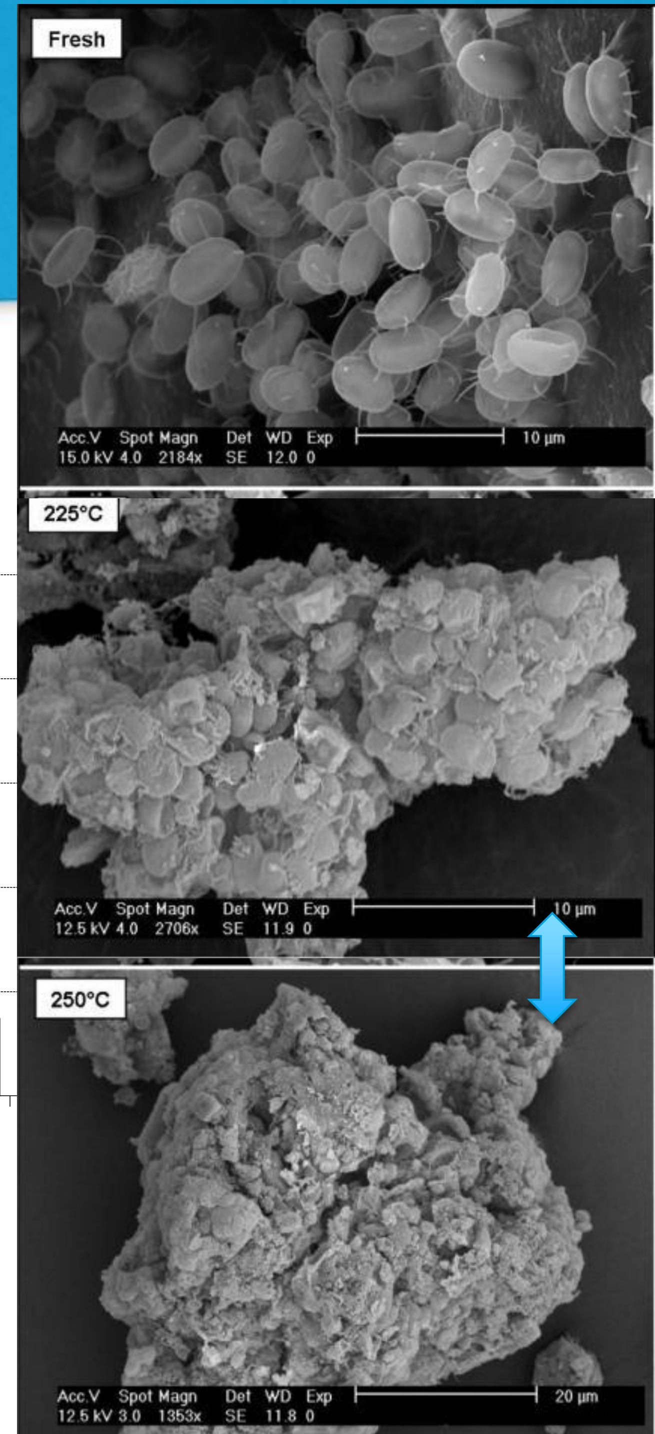



*Liquefaction & CW hydrolysis kinetics*

*Gasification to $C_xH_y$ and $H_2$*

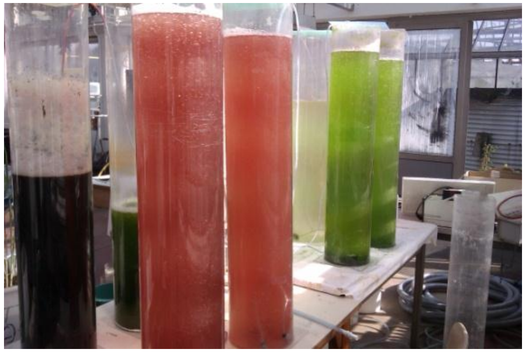
# Solid residue



# Effect of algae strain

## USING SAME PROCESS EQUIPMENT AND SAME EXPERIMENTAL PROCEDURES



- *Nannochloropsis gaditana*
- *Tetraselmis suecica*
- *Scenedesmus obliquus*
- *Scenedesmus almeriensis*
- *Porphyridium purpureum*
- *Chlorella vulgaris*
- *Phaeodactylum tricornutum*
- *Dunaliella tertiolecta*

| Strain | Ash | Lipids | Proteins | Carb* | N | C | H | O* |
|---|---|---|---|---|---|---|---|---|
| *S. obliquus* | 13.2% | 16.8 | 48.8 | 19.3 | 7.8 | 48.4 | 6.2 | 22.6 |
| *P. tricornutum* | 14.5% | 21.9 | 48.3 | 15.1 | 7.7 | 48.2 | 6.6 | 22.8 |
| *N. gaditana* | 17.5% | 25.1 | 47.5 | 9.2 | 7.6 | 46.9 | 6.2 | 21.1 |
| *S. almeriensis* | 6.8% | 21.8 | 50.0 | 22.0 | 8.0 | 53.1 | 6.8 | 25.7 |
| *T. suecica* | 18.4% | 19.5 | 38.0 | 23.6 | 6.1 | 45.2 | 6.2 | 23.6 |
| *P. purpureum* | 17.8% | 12.1 | 48.9 | 20.4 | 7.8 | 44.3 | 5.8 | 23.4 |
| *C. vulgaris* | 10.2% | 20.4 | 51.7 | 17.1 | 8.3 | 50.2 | 6.5 | 24.2 |
| *D. tertiolecta* | 6.4% | 23.4 | 55.6 | 14.5 | 8.9 | 51.4 | 6.6 | 26.6 |

* by difference

(Lopez Barreiro et al, 2013)

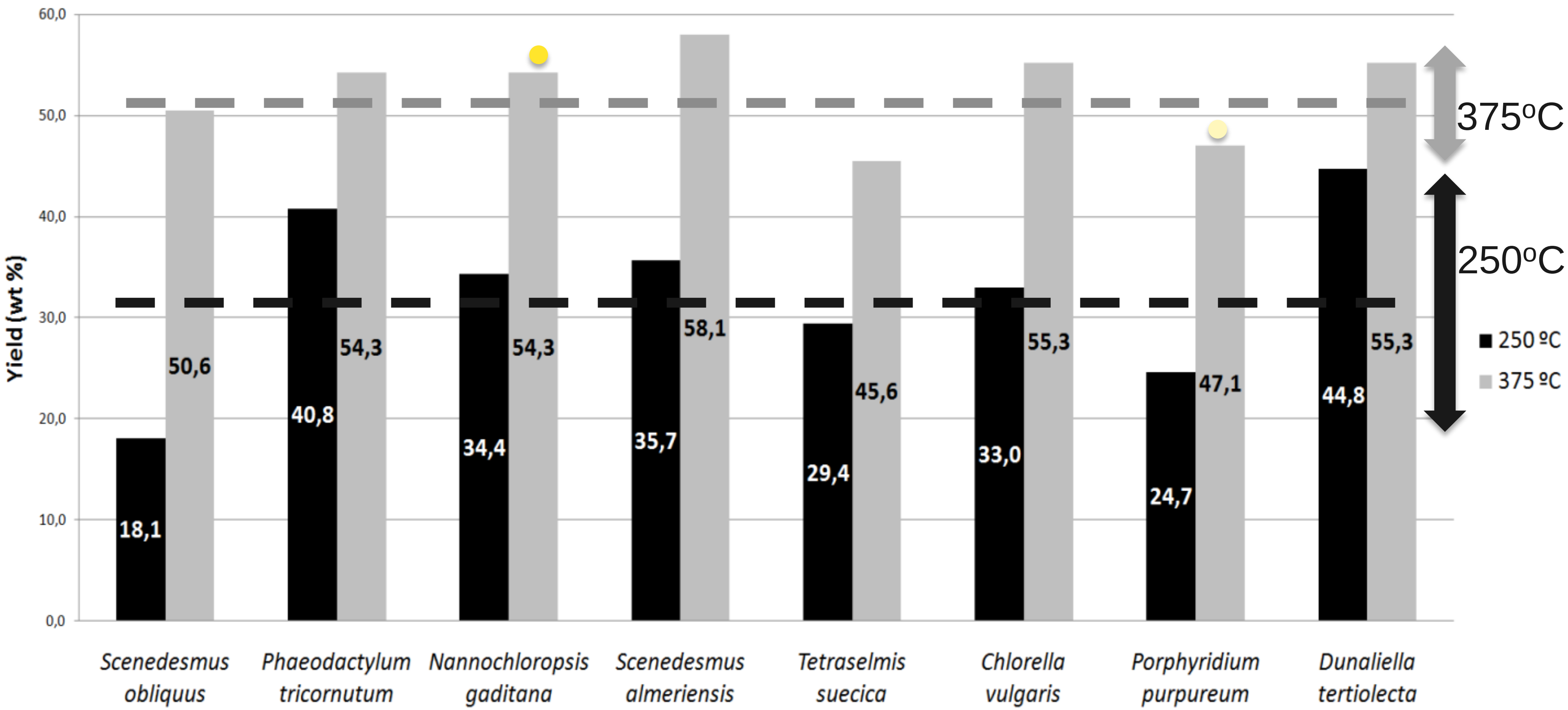
# Effect of algae strain - RESULTS

**USING SAME PROCESS EQUIPMENT AND EXPERIMENTAL PROCEDURES**

*(Lopez Barreiro et al, 2013)*

At 375ºC: limited effect of strain — - no strong effect of marine vs. fresh
- high lipid content not required

250ºC: significant differences !



# Contents



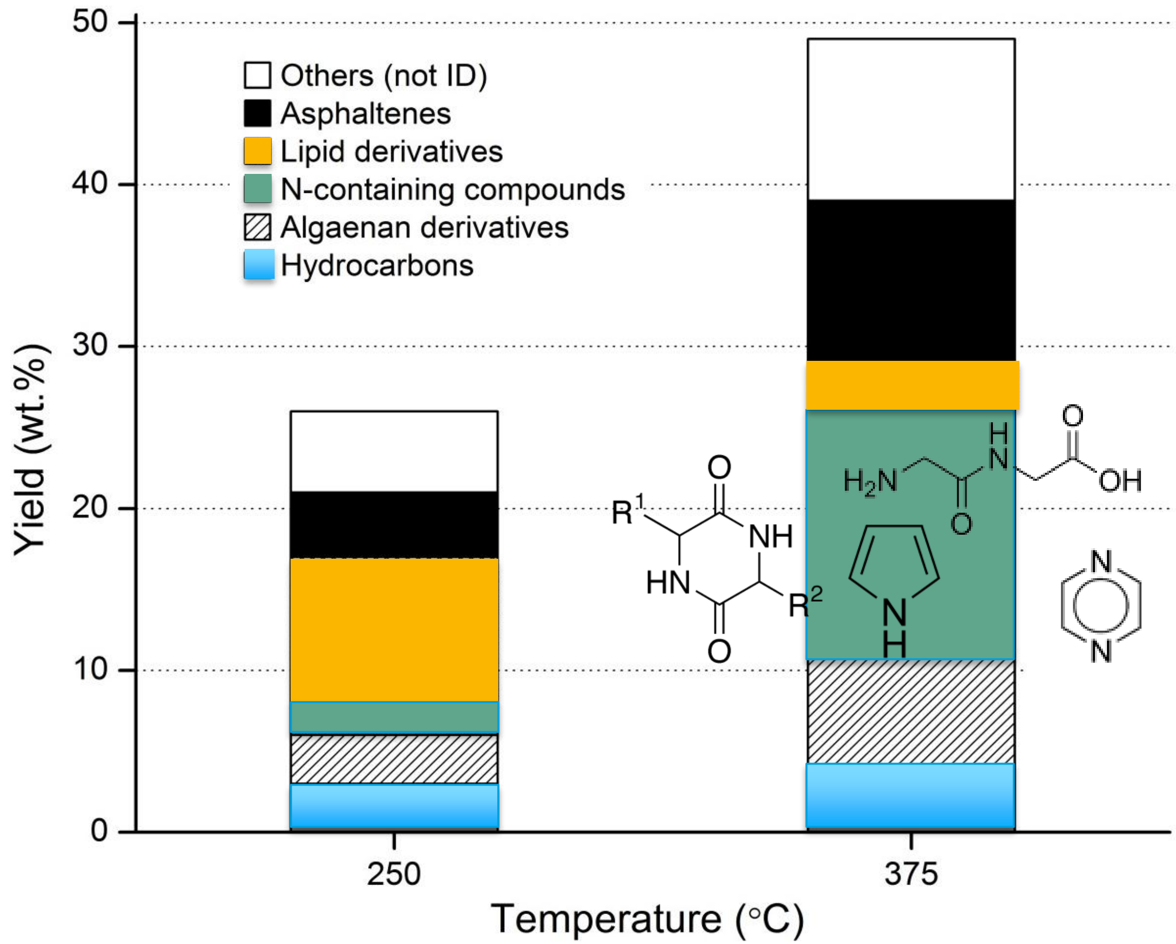
Over 400 compounds identified using stepwise TGA/Py-SPME-GC-MS

*(Torri et al, 2012); (Garcia Alba et al, 2013)*

# Biocrude – upgrading

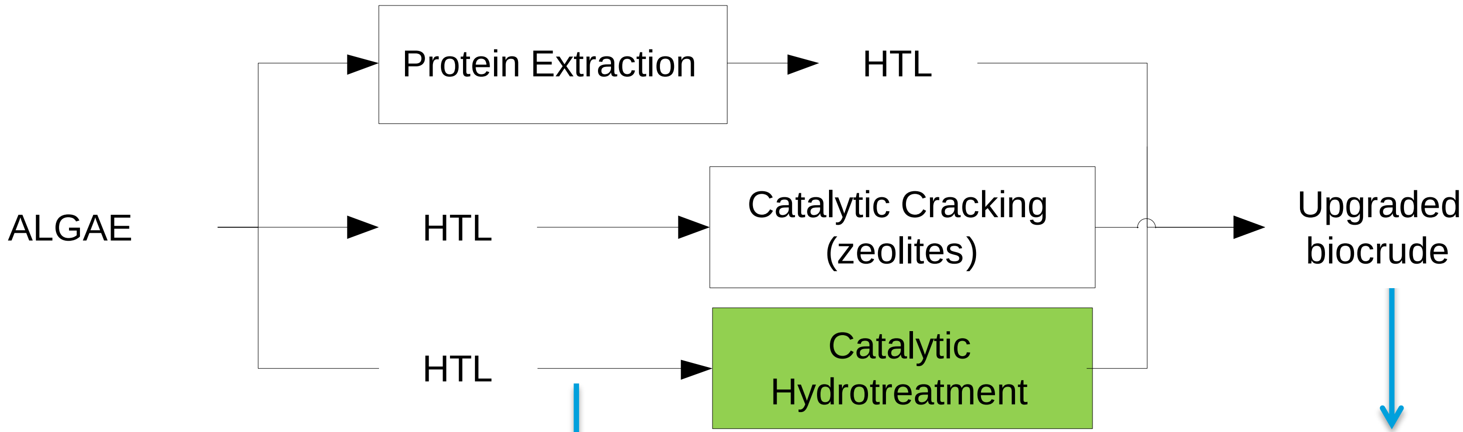
+ High biocrude yields (50%) and Energy recovery (75%)

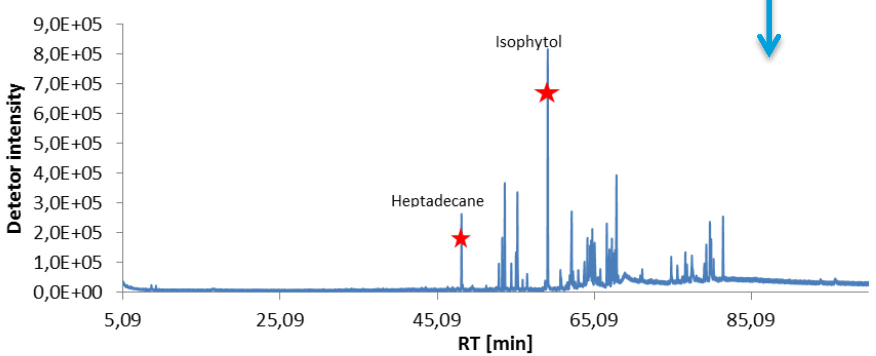
- N-content of oil increases with oil yield & energy recovery

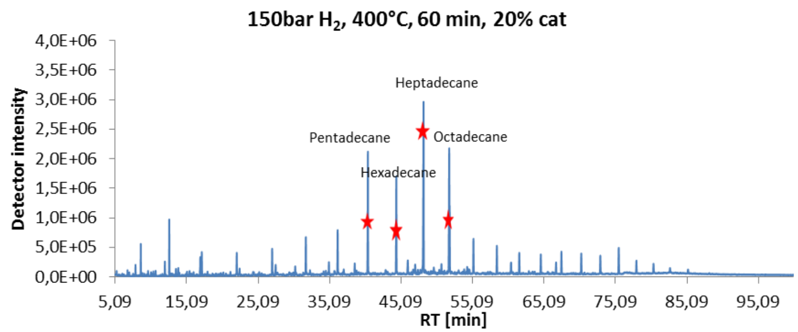


# R&D efforts to improve oil properties

## Reduction of N-content, O-content, viscosity  (1)



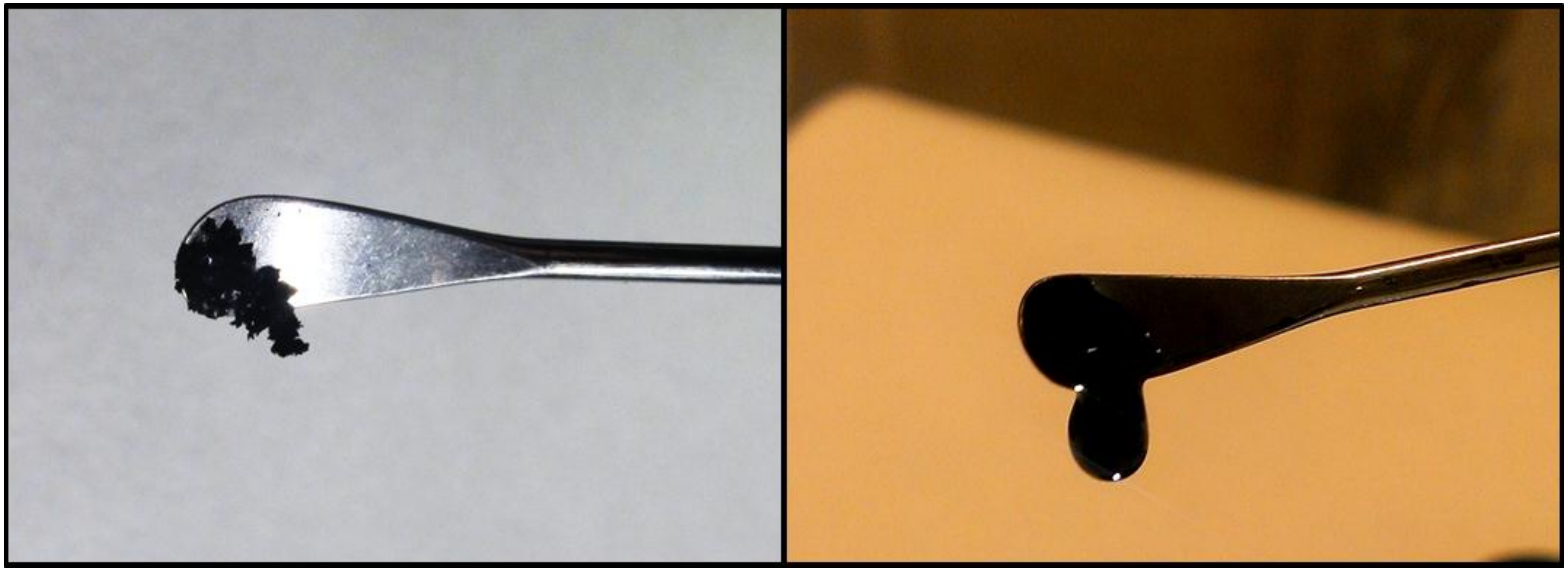




| Sample | Elemental composition wt.% | | | | HHV |
|---|---|---|---|---|---|
| | C | H | N | O | (MJ/kg) |
| **HTL 350°C, 5 min** | 74.48 | 8.99 | **6.86** | **9.67** | 36.0 |
| **150 bar $H_2$, 400°C , 60 min, no cat.** | 84.54 | 11.29 | **2.68** | **1.50** | **42.8** |
| **150 bar $H_2$, 400°C , 60 min, with cat.** | 84.92 | 12.20 | **2.06** | **0.82** | **44.1** |

(Garcia Alba, thesis 2013)

# R&D efforts to improve oil properties

Reduction of N-content, O-content, viscosity (2)



(Garcia Alba, 2013)

By hydrotreating 350ºC HTL oil :

O-level and N-level reduced to 1-2%

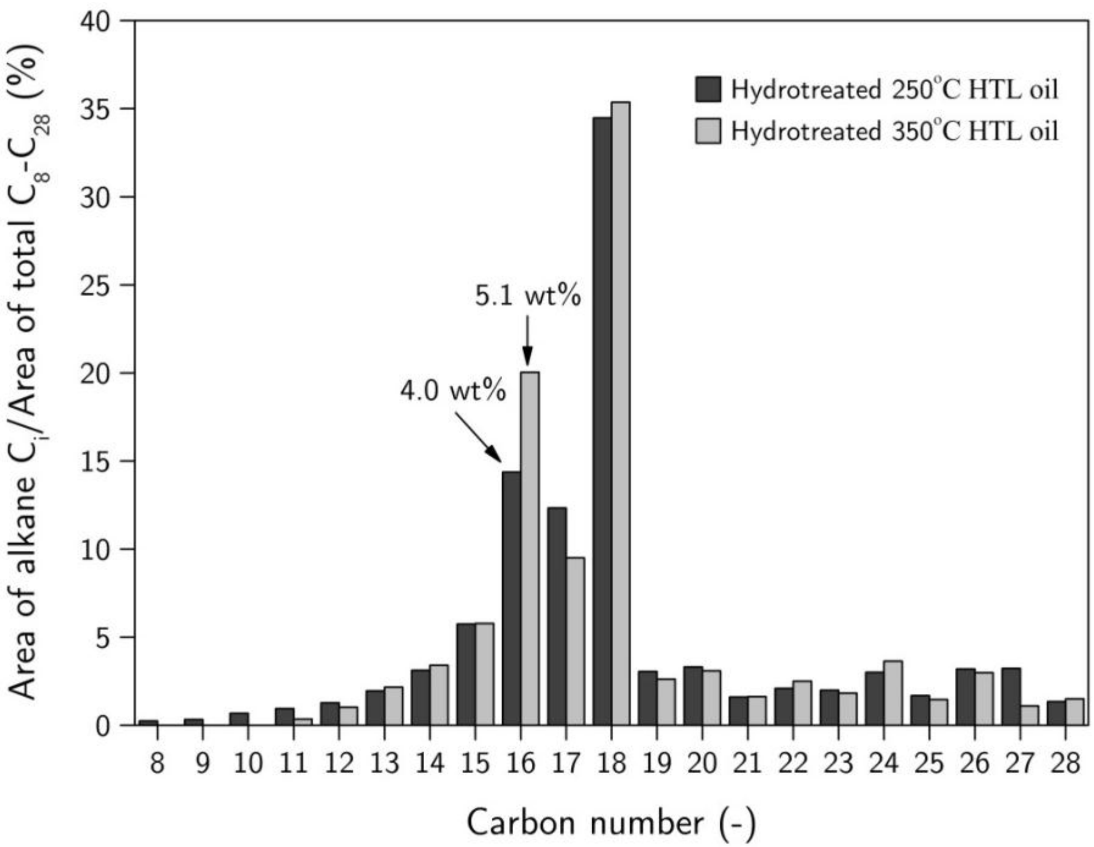
viscosity reduced, coking tendency (MCRT value) is very low

Co-processing in existing Refineries (economy of scale!) seems a feasibile route !

N-content is possibly a critical issue

# Applicability hydrotreated HTL oils

Desmodesmus Sp., HTL + H2 treatment




Around 20wt% of the oil
is already a hydrocarbon fraction

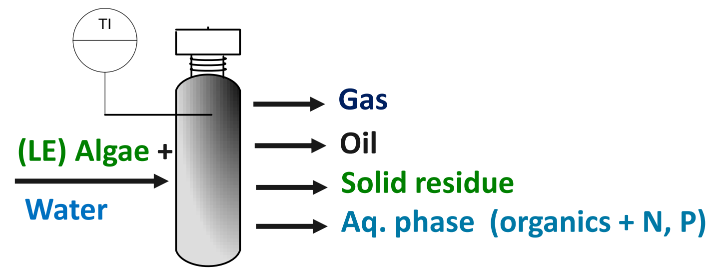
=> ‘drop-in’ fuel-fraction ?

(Garcia Alba, thesis 2013)

# Contents



# HTL integration - Trends




- HTL as part of biorefinery schemes
- HTL works on whole algae & on lipid extracted residue streams => wet extraction technologies

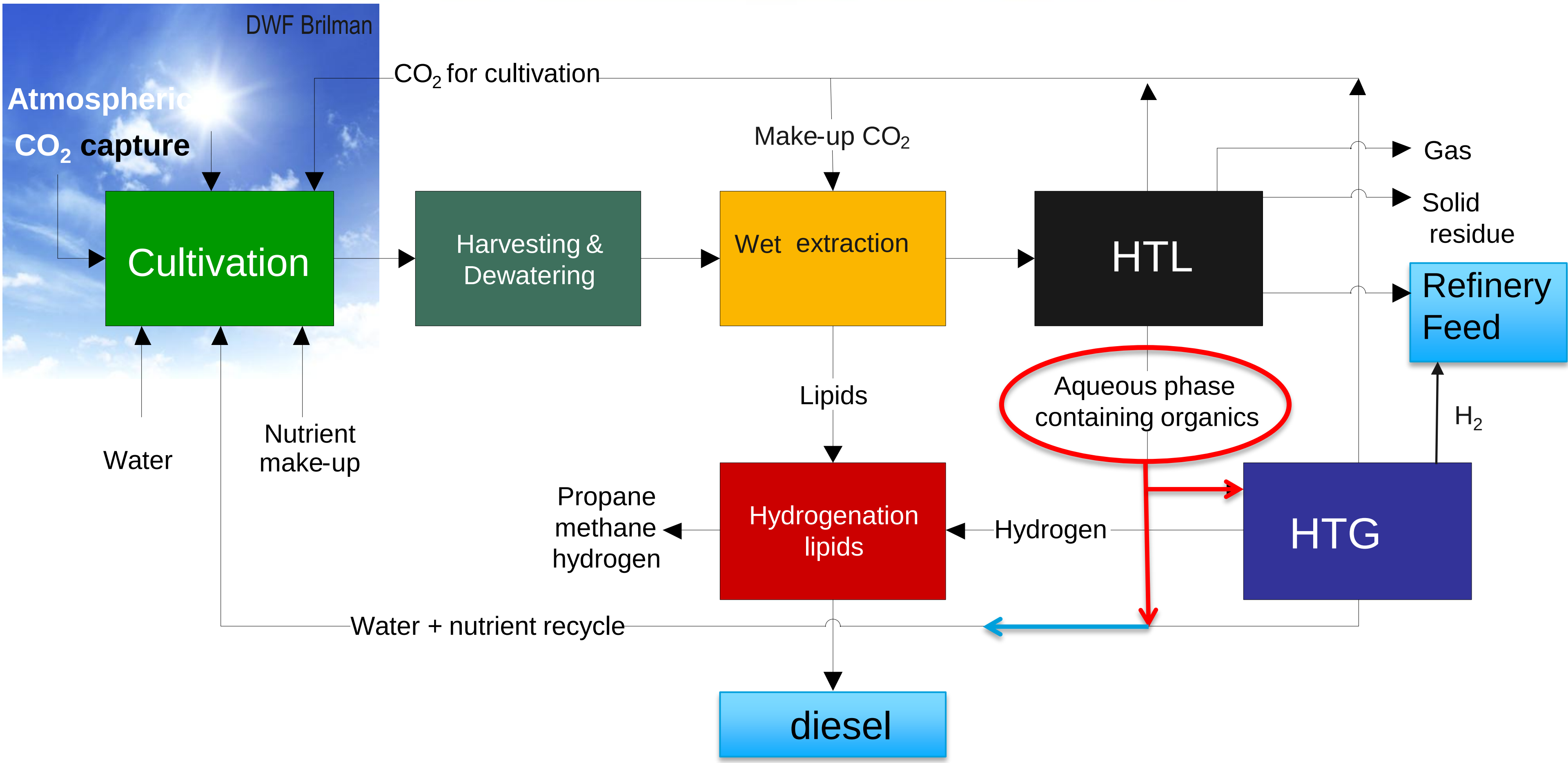
- Aqueous Phase ex-HTL is still 'contaminated'
  => nutrients recovery & water treatment

- Continuous operation
  - Optimizing process conditions
  - pumping, heat exchange, phase separation

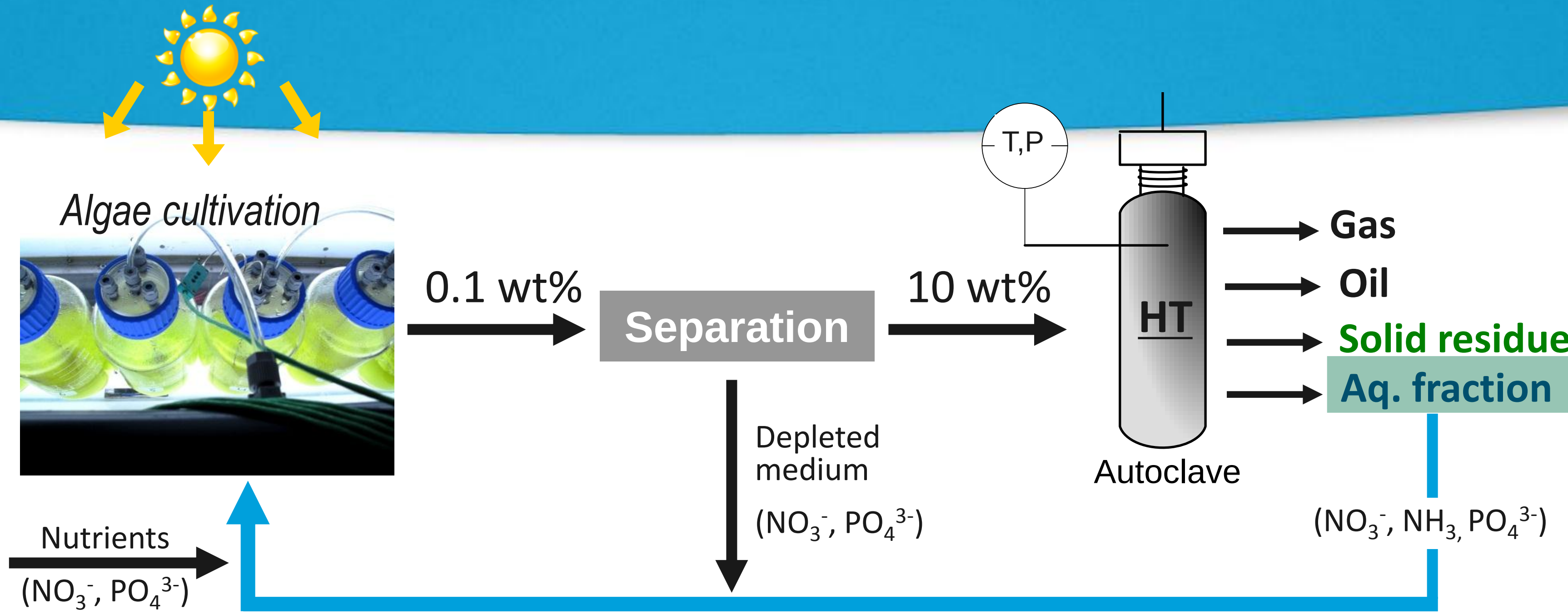
also:
- Large scale demo's & commercialisation

# HTL in an integrated Algae-to-Fuels (bio-)refinery concept

## Closing the Cycles and Process Evaluation



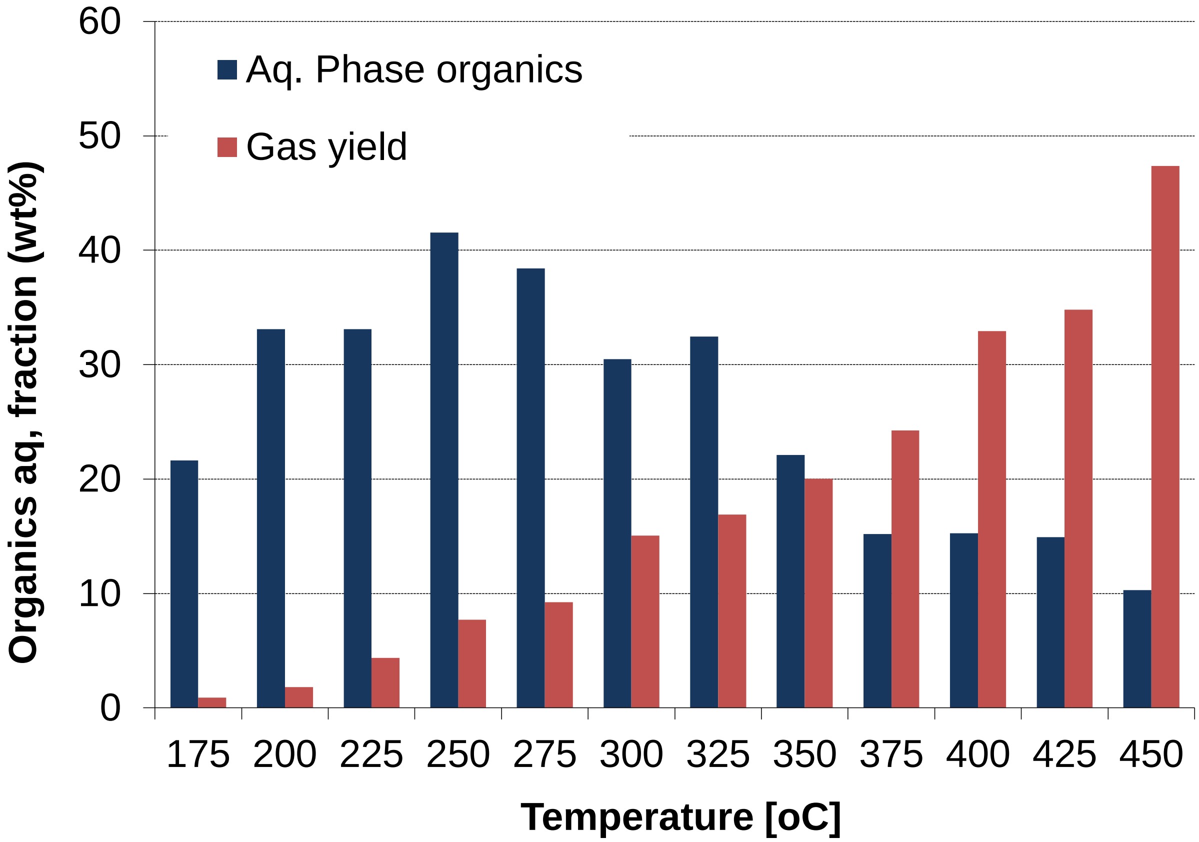
# (1) Direct recycling of HTL aq.phase




- 5 cycles test successfully completed
- No adverse effects on growth rate
- Algae changed their appearance during test


(Garcia Alba, Chem.Sus.Chem, 2013)

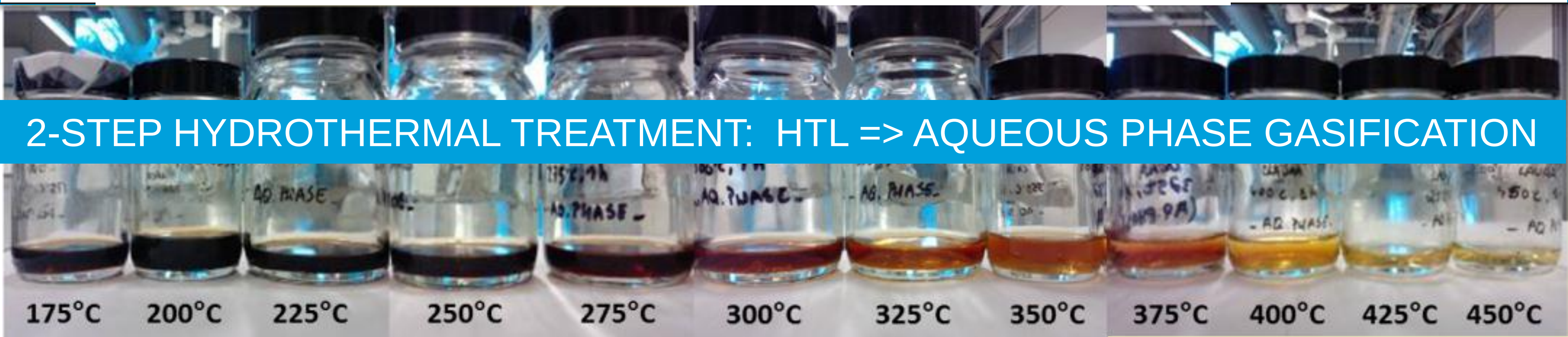
# (2) Hydrothermal Gasification of the Aqueous Phase




Production of esp.

- $CO_2$ (to cultivation)
- $H_2$ (oil upgrading)
- Fuel gas (heat)

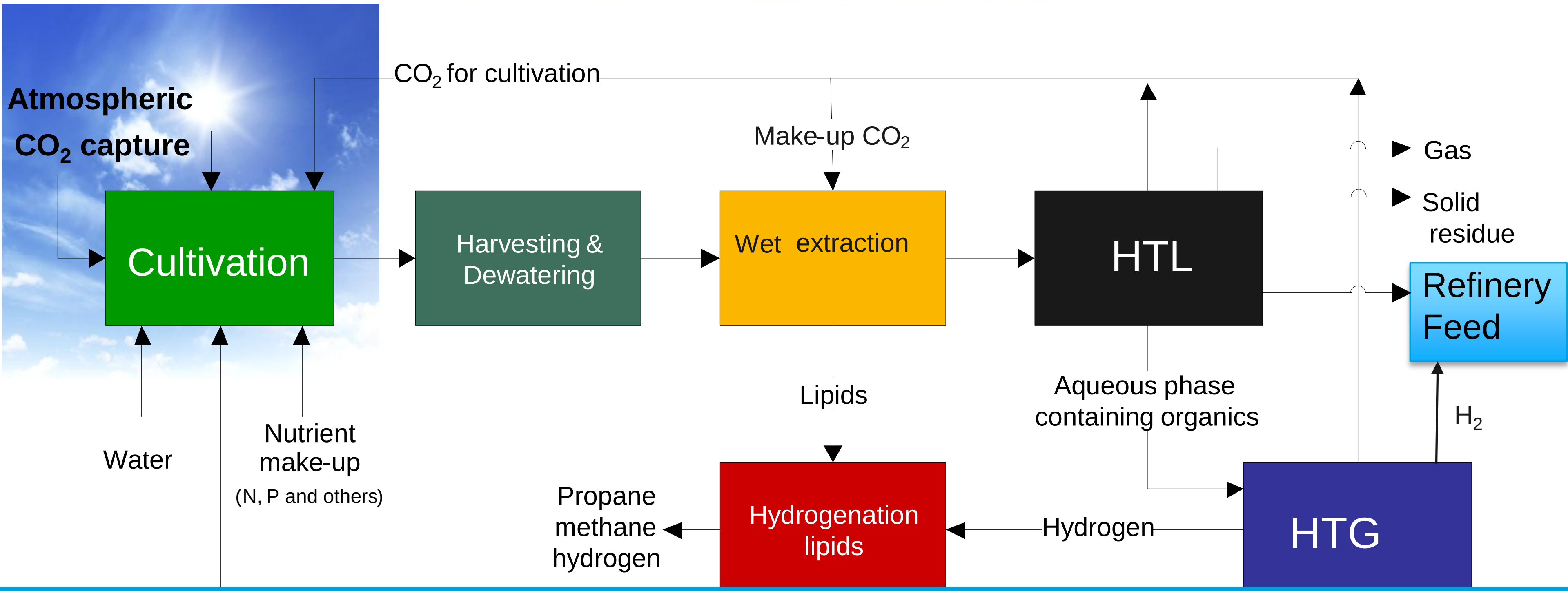
Hydrothermal Gasification of <u>whole</u> microalgae: incomplete, complex and likely to be uneconomical *(Chakinala et al.,2010)*




2-STEP HYDROTHERMAL TREATMENT: HTL => AQUEOUS PHASE GASIFICATION

# HTL in an integrated Algae-to-Fuels (bio-)refinery concept

## PROCESS EVALUATION…




**Total Energy yield**: 22 GJ / ton dry algae

| Algae with | [25% lipids] |
|---|---|
| diesel (lipid based) | 42% |
| Refinery Feed (biocrude) | 44% |
| Fuel gas; ($CH_4$, excess $H_2$) | 12% |

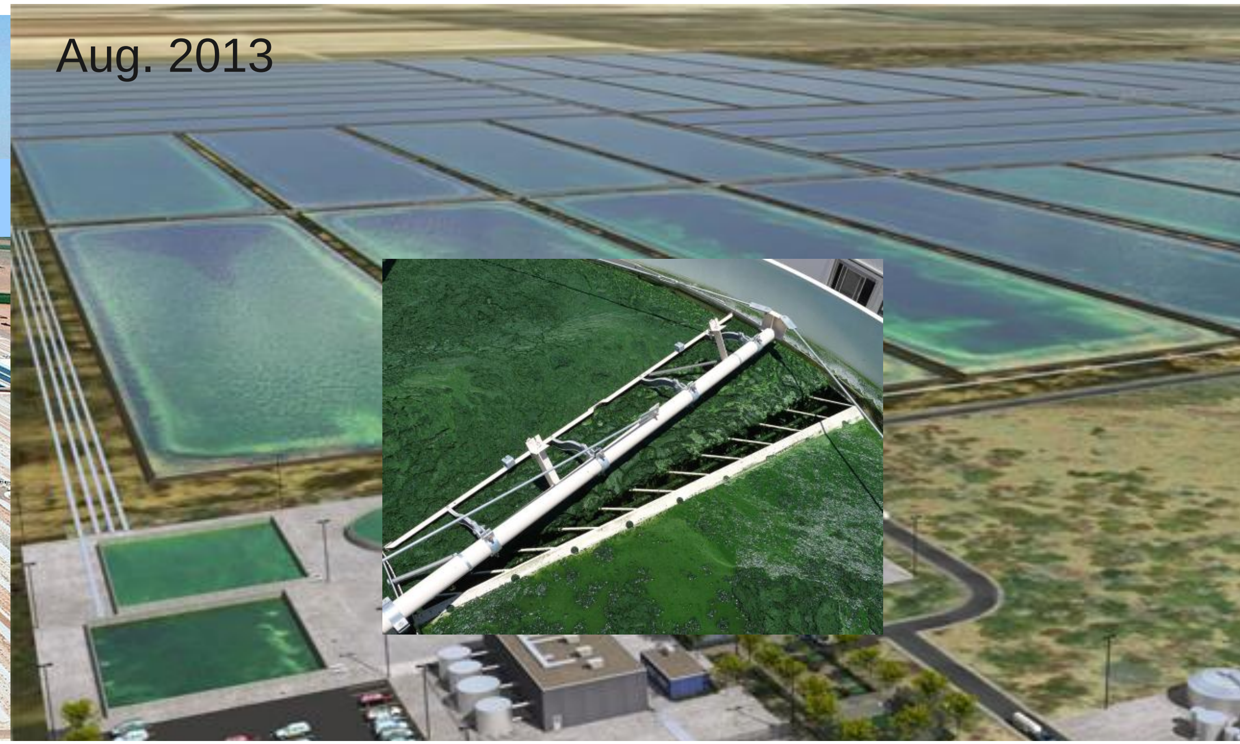
**Fossil Energy Ratio:**
**Energy out / Energy in**

**2.2**

Net Energy Production !!!

# HTL for Algae to Fuels ….. Realistic ?

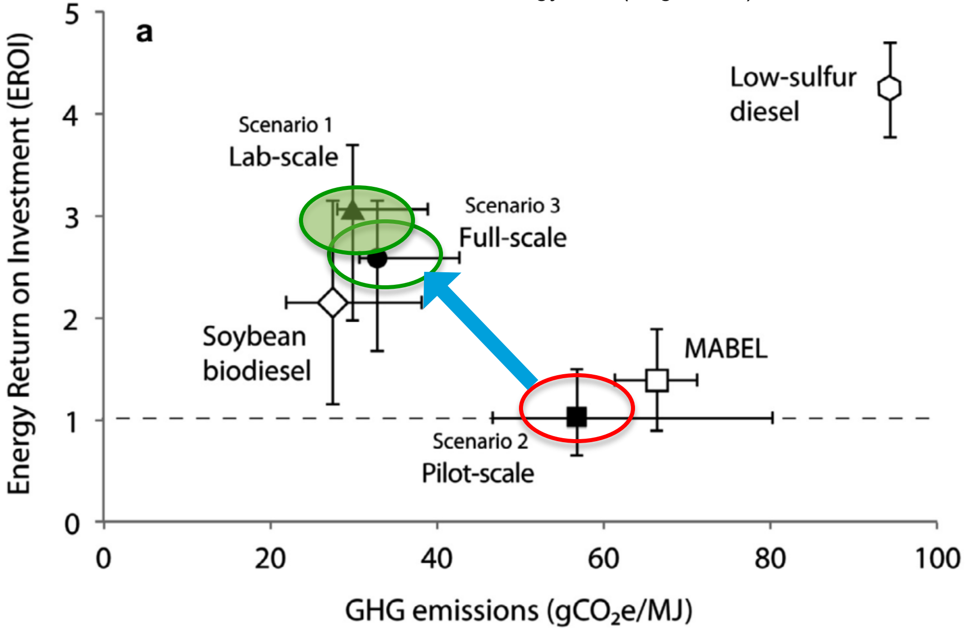
**Example: Sapphire Energy** (USA) - Green Crude - to Refinery ; 100 acres; target 5000 barrels/day in 2018


*"The green crude production chain fits neatly into the current energy infrastructure and is therefore an exceptionally promising, environmentally friendly raw material for industry"*

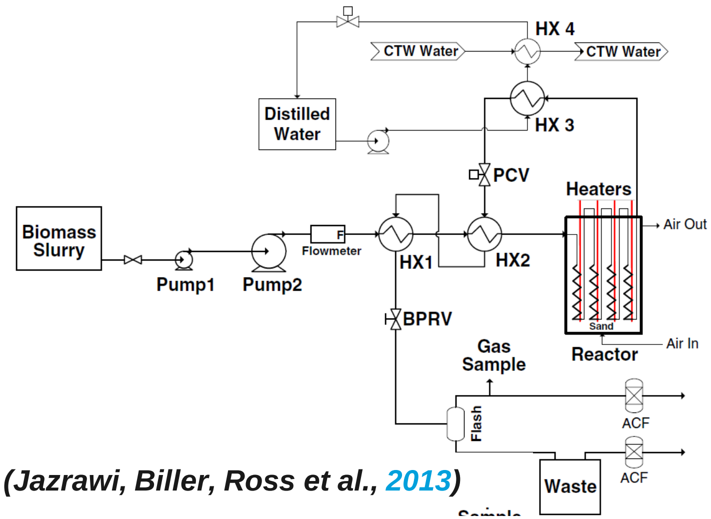
# Recent LCA study for Sapphire Energy plant

*Liu et al., Bioresource Technology 148 (aug. 2013) 163–171*

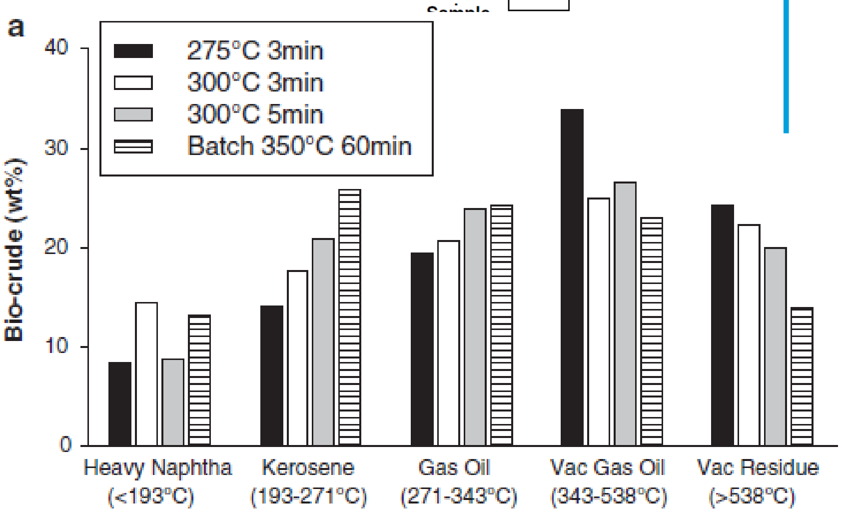


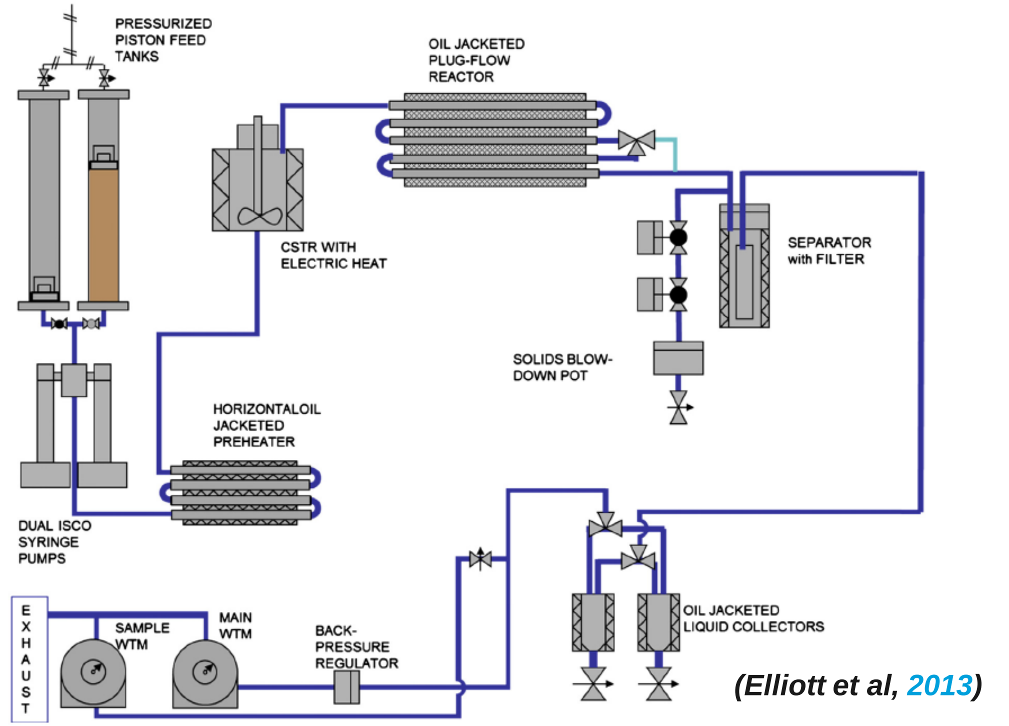

| | Energy OUT / IN (FER) |
|---|---|
| *Algae-to-Fuels (UT)* | 2.2 |
| Sapphire Energy Inc.: | 2.5 (full scale) |
| Sapphire Energy Inc.: | 170 kg $CO_2$/bbl |
| | ≈ 71 g $CO_2$ / km (1:15) |

- “Algae to Fuels” via Biocrude (‘Refinery Feed’) is a net energy producer !
- Comparing Pilot Scale with lab- and full-scale; biocrude yield 20 wt% on pilot scale vs. 50 wt% on lab scale (and expected for full scale).
  => Many (engineering) challenges still need to be solved




*(Jazrawi, Biller, Ross et al., 2013)*




*(Elliott et al, 2013)*

*(U. Twente, NL)*

**2013: HTL publications…more focus on continuous operation / pilot plant**

# SUMMARY

- ALGAL BIOMASS
  - C-NEUTRAL
  - FUELS, FEED & CHEMICALS
  - SECURITY OF SUPPLY
- HTL OF MICROALGAE
  - NO DRYING, NO GRINDING
  - 'PLATFORM': BIOCRUDE 'ECONOMY OF (REFINERY) SCALE'
  - ENERGY RECOVERY: > 75%
  - NUTRIENT RECYCLE VIA AQ.PHAS
- R&D CHALLENGES
  - LIQUEFACTION FUNDAMENTALS
  - N-REDUCTION OF OIL
  - AQ.PHASE TREATMENT
  - PROCESSING CONC.SLURRIES HEAT EXCHANGE, PUMPING, SALTS/SOLIDS HANDLING
  - PHASE SEPARATION
  - CLOSING RECYCLES
  - SCALE-UP ISSUES
- INTEGRATED SYSTEMS
- CHAIN EVALUATION

# Conclusions & Outlook

**HTL of microalgae**

**… is not likely to strand in the pilot-phase on technology aspects**
**but considerable R&D effort is still needed**

**… enables Algae to Fuels to become reality**
**esp. if cultivation costs can be reduced**
**& HTL can help in this ! (nutrients recycle)**

**HTL – a future "unit operation" in biorefineries ?**

# Thank you !

**More info ?**

**wim.brilman @ utwente.nl**

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Cristian Torri
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## More info ?

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